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# CONTENTS

## PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY.

	PAGE
CLXXVI.—Contributions to the Chemistry of the Terpenes. Part XX. The Action of Hypochlorous Acid on Pinene. By GEORGE GERALD HENDERSON and JOSEPH KENNETH MARSH	1492
CLXXVII.—The Reactivity of Doubly-conjugated Unsaturated Ketones. Part I. 4'-Dimethylamino-2-hydroxydistyryl Ketone. By ISIDOR MORRIS HEILBRON and JOHANNES SYBRANDT BUCK	1500
CLXXVIII.—The Reactivity of Doubly-conjugated Unsaturated Ketones. Part II. The Action of Hydroxylamine, Semicarbazide, and Phenylhydrazine on 4'-Dimethylamino-2-hydroxydistyryl Ketone and its Methyl Ether. By ISIDOR MORRIS HEILBRON and JOHANNES SYBRANDT BUCK	1515
LXXIX.—Surface Tensions of Salts of the Fatty Acids and their Mixtures. By ERIC EVERARD WALKER	1521
CLXXX.— <i>ortho</i> -Chlorodinitrotoluenes. Part III. Bases derived from 2-Chloro-4:5-dinitrotoluene. By GILBERT T. MORGAN and WILLIAM ARTHUR PERCIVAL CHALLENGOR	1537
LXXXI.—Non-aromatic Diazonium Salts. Part VII. The Diazo-reaction in the <i>iso</i> Oxazole Series. By GILBERT T. MORGAN and HENRY BURGESS	1546
LXXXII.—A New Type of Iodine Compound. By JOHN NORMAN COLLIE and AMY ADA BEATRICE REILLY	1550
Photosynthetic Processes in the Air, upon the Land, and in the Sea in Relation to the Origin and Continuance of Life on the Earth. Hugo Müller Lecture, Delivered before the Chemical Society on June 16th, 1921. By BENJAMIN MOORE, D.Sc., F.R.S.	1555
XXXIII.—The <i>ortho</i> -Dimethylantraquinones and their Derivatives. By ARTHUR FAIRBOURNE	1573
XXXIV.—Experiments on the Synthesis of the Polyacetic Acids of Methane. Part III. Conditions controlling Synthesis by the Cyanoacetic Ester Method—( <i>continued</i> ). By CHRISTOPHER KELK INGOLD and EDWARD ARTHUR PERREN	1582

	PAGE
CLXXXV.—Harmine and Harmaline. Part V. The Synthesis of Norharman. By WILLIAM OGILVY KERMAK, WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON.	1602
CLXXXVI.—The Molecular Conductivity of some Sulphonium Compounds in Acetone. By SIR PRAPHULLA CHANDRA RÂY and KALIKUMAR KUMAR . . . . .	1643
CLXXXVII.—The Essential Oil from <i>Andropogon ivarancusa</i> , Jones, and the Constitution of Piperitone. By JOHN LIONEL SIMONSEN . . . . .	1644
CLXXXVIII.—The Calculation of the Colour of "Cyclic" Coloured Substances. By JAMES MOIR . . . . .	1654
CLXXXIX.—The Hydration of the Fibres of Soap Curd. Part III. Sorption of Sodium Palmitate. By MARY EVELYN LAING . . . . .	1669
CXC.—The Propagation of Flame in Mixtures of Ethylene and Air. By WILLIAM RONALD CHAPMAN . . . . .	1677
CXCI.—The Effect of Temperature on Platinum Black and other Finely-divided Metals. By ROBERT WRIGHT and ROBERT CHRISTIE SMITH . . . . .	1683
CXCII.—Physical Chemistry of the Oxides of Lead. Part I. The Solubility of Lead Monoxide. By SAMUEL GLASTONE . . . . .	1689
CXCIII.—The Mechanism of the Action of Fused Alkalis. Part II. The Action of Fused Potassium Hydroxide on Phenylglyceric Acid. By (the late) HENRY RONDEL LE SUEUR and CYRIL CHRISTIAN WOOD . . . . .	1697

## INDEX OF AUTHORS' NAMES

### IN TRANSACTIONS AND ABSTRACTS.

ALESSANDRI, L., i, 730.	Barborovský, J., and V. Hanák, ii, 573.
Allmand, A. J. See H. T. S. Britton.	Barlot, J. See (Mlle) Mouret.
Angelis, M. de, i, 73 <sup>1</sup>	Bartels, H., ii, 565.
Ariano, R., ii, 580.	Bassi, G. See G. Poma.
Armstrong, E. F., and T. P. Hilditch, ii, 582.	Bauriedel, G. See W. Dilthey.
Arreguine, V., and E. D. García, ii, 605.	Bechhold, H., and S. M. Neuschloss, i, 705.
Aston, F. W., ii, 565.	Behr, H. See W. Borsche.
Aubel, E. See L. Blum.	Belladen, L., ii, 588.
Aubel, E. van, ii, 575.	Bergholm, C., ii, 568.
Auslaender, F. See E. Philippi.	Bergmann, M., i, 707.
BAGIELLA, E. See M. Giua.	Berndt, A. See J. Tröger.
Balareff, D., ii, 575.	Bertrand, G., and (Mme) M. Rosenblatt, i, 759.
Bamberger, E., i, 716, 723.	Bezssonoff, N., ii, 608.

- Bielous, E., i, 712.  
 Blum, L., and E. Aubel, i, 756.  
 Hoedeker, E. See E. Heuser.  
 Borsche, W. [with H. Behr and H. Wieckhorst], i, 729.  
 Bradford, S. C., ii, 577.  
 Bregenzner, A. See E. Knoevenagel.  
 Bretschneider, R. See H. Ost.  
 Briggs, S. H. C., ii, 583.  
 Brill, H. C., i, 727.  
 Brinton, P. H. M.-P., F. N. Schertz, W. G. Crockett, and P. P. Merkel, ii, 592.  
 Britton, H. T. S., and A. J. Allmand, ii, 588.  
 Bruhns, G., ii, 592.  
 Brulé, M., and H. Garban, i, 755.  
 Bruni, G., and E. Romani, i, 734.  
 Buck, J. S. See I. M. Heilbron.  
 Burger, B. See W. Dilthey.  
 Burgess, H. See G. T. Morgan.  
 Burrows, G. J., and E. E. Turner, i, 712, 751.  
 Butler, G. S. See H. B. Dunncliff.  
 CALDERARO, E. See E. Oliveri-Man-dalà.  
 Carighelli, R. See L. Maquenne.  
 Cornatesco, R., ii, 576.  
 Challenor, W. A. P. See G. T. Morgan.  
 Chapin, R. M., ii, 598, 599.  
 Chapman, W. R., TRANS., 1677.  
 Chaudron, G., ii, 584.  
 Christman, A. A., and H. B. Lewis, i, 755.  
 Jusa, R., i, 749.  
 Clarke, J. R., ii, 569.  
 Clifford, W. M., ii, 604.  
 Clogne, R., and J. Réglade, i, 754.  
 Coffey, S., i, 706.  
 Cohen, J. B. See V. Froelicher.  
 Colin, H., ii, 607.  
 Collie, J. N., and A. A. B. Reilly, TRANS., 1550.  
 Cornubert, R., i, 730.  
 Crockett, W. G. See P. H. M.-P. Brinton.  
 Crommelin, C. A., ii, 573.  
 Curtius, T., and F. W. Haas, i, 747.  
 Cuy, E. J., ii, 584.  
 DATTA, S., ii, 570.  
 Dejean, P., ii, 573.  
 Delépine, M., ii, 567.  
 Demoussy, E. See L. Maquenne.  
 Desvergnes, L., ii, 600.  
 Dieckmann, T., ii, 597.  
 Dilthey, W. [with G. Bauriedel, B. Burger, G. Geisselbrecht, F. von Ibach, F. Kiefer, A. Seeger, O. Simon, R. Taucher, and J. Winkler], i, 735.  
 Dobbie, (Sir) J. J., and J. J. Fox, ii, 566.  
 Dohme, A. R. L., ii, 604.  
 Doisy, E. A., and E. P. Eaton, i, 753.  
 Donard, E. See E. Fourneau.  
 Donleavy, J. J. See A. J. Hill.  
 Dox, A. W., and L. Yoder, i, 740.  
 Dudley, H. W., and C. L. Evans, i, 749.  
 Dunncliff, H. B., and G. S. Butler, i, 705.  
 EATON, E. P. See E. A. Doisy.  
 Eddy, W. H., H. L. Heft, H. C. Stevenson, and R. Johnson, i, 758.  
 Edie, E. S., i, 750.  
 Emery, W. O., ii, 603.  
 Engel, E. See H. Franzen.  
 Erlich, J., ii, 580.  
 Evans, C. L. See H. W. Dudley.  
 FAIRBOURNE, A., TRANS., 1573.  
 Farbenfabriken vorm. F. Bayer & Co., i, 747.  
 Farbwerke vorm. Meister, Lucius, & Brüning, i, 752.  
 Finkelstein, J. L. See R. M. Wilhelm.  
 Florence, G. See L. Hugouenq.  
 Foote, P. D. See F. L. Mohler.  
 Fourneau, E., and E. Donard, ii, 584.  
 Fox, J. J. See Sir J. J. Dobbie.  
 Franco, C. See U. Sborgi.  
 Franzen, H., and E. Engel, i, 713.  
 Franzen, H., and F. Helwert, i, 714.  
 Frese, W., ii, 569.  
 Fresenius, W., and L. Grünhut, ii, 602.  
 Froboese, V., ii, 592.  
 Froelicher, V., and J. B. Cohen, i, 728.  
 Fry, W. H. See C. J. Moore.  
 GALLAGHER, P., i, 715.  
 Garban, H. See M. Brulé.  
 García, E. D. See V. Arreguine.  
 Garnier. See P. Pascal.  
 Gault, H., and R. Weick, i, 728.  
 Gehroke, E., and E. Lau, ii, 565.  
 Geisselbrecht, G. See W. Dilthey.  
 Gellenden, W. See B. Neumann.  
 General Electric Co., Ltd., Research Staff, ii, 591.  
 Gerhardt, O., i, 746.  
 Gerold, E., ii, 585.  
 Giua, M., i, 712.  
 Giua, M., and E. Bagiella, i, 730.  
 Glasstone, S., TRANS., 1689.  
 Graham, H., and A. K. Macbeth, ii, 567.  
 Gratia, A., i, 753.  
 Greaves, J. E., and Y. Lund, i, 758.  
 Griebel, C., ii, 606.  
 Grünhut, L., ii, 602.

- Grünhut, L. See also W. Fresenius.  
Guertler, W., and K. L. Meissner,  
ii, 589.
- HAACKH, H., i, 729.  
Haas, F. W. See T. Curtius.  
Haeahn, H., ii, 579.  
Haggard, H. W., and Y. Henderson,  
i, 752.  
Hahn, F. von, ii, 577.  
Haller, R., ii, 576.  
Hamer, (Miss) F. M., i, 738.  
Hanák, V. See J. Barborovský.  
Harkins, W. D., ii, 582.  
Harst, J. C. van der, and C. H. Koers,  
ii, 601.  
Heft, H. L. See W. H. Eddy.  
Heilbron, I. M., and J. S. Buck,  
TRANS., 1500, 1515.  
Helwert, F. See H. Franzen.  
Henderson, G. G., and J. K. Marsh,  
TRANS., 1492.  
Henderson, Y. See H. W. Haggard.  
Henstock, H., i, 713.  
Herrdegen, L. See E. Müller.  
Herz, W., ii, 573.  
Hess, A. F., G. F. McCann, and  
A. M. Pappenheimer, i, 757.  
Hess, K., W. Wittelsbach, and E.  
Messmer, i, 710.  
Heuser, E., and E. Boedeker, i, 708.  
Hickinbottom, W. J. See J. Reilly.  
Hilditch, T. P. See E. F. Armstrong.  
Hill, A. J., and J. J. Donleavy, i, 714.  
Hodges, E. R., ii, 589.  
Hofmann-Meyer, A. See H. Meyer.  
Hughes, W., ii, 573.  
Hugoumeng, L., and G. Florence,  
i, 711.  
Hynes, W. A. See C. P. Sherwin.
- IBACH, F. von. See W. Dilthey.  
Ingold, C. K., and E. A. Perren,  
TRANS., 1582.  
Ishikawa, S., i, 728.  
Itagaki, T. See Y. Murayama.  
Itallie, L. van, and A. J. Steenhauer,  
ii, 607.
- JOHNSON, E., ii, 605.  
Johnson, R. See W. H. Eddy.  
Jones, M. R., and L. L. Nye, i, 753.  
Jonesco, S., i, 760.
- KARRER, P., i, 707.  
Keffler, L. P. G., i, 739.  
Kennall, E. C. See A. E. Osterberg.  
Kenne, J., and E. Witham, i, 731.  
Kermack, W. O., W. H. Perkin, jun.,  
and R. Robinson, TRANS., 1602.  
Kiefer, F. See W. Dilthey.  
Kinder, H., ii, 594.  
King, H., i, 751.
- Knoevenagel, E., and A. Bregenzner,  
i, 709, 710.  
Knoevenagel, E., and R. Motz, i, 709.  
Koelsch, H., ii, 597.  
Koers, C. H. See J. C. van der Harst.  
König, W., and O. Treichel, i, 738.  
Kolkwitz, R., i, 757.  
Kotyga, G. See B. Neumann.  
Kramer, B., and F. F. Tisdall, ii, 595.  
Kremers, E., and R. Kremers, i, 705.  
Kremers, R. See E. Kremers.  
Krishna, S., i, 735.  
Kruyt, H. R., ii, 577.  
Kumar, K. See (Sir) P. C. Rây.
- LABOURRASSE. See P. Pascal.  
Ladenburg, R., ii, 567.  
Laing, (Miss) M. E., TRANS., 1669.  
Langfeldt, E., i, 754.  
Lau, E. See E. Gehreke.  
Lebeau, P., and M. Picon, ii, 591.  
Legg, D. A. See C. W. Weizmann.  
Lenz, E., i, 756.  
Le Sueur, H. R., and C. C. Wood,  
TRANS., 1697.  
Levi, G. R., ii, 599.  
Lewis, H. B. See A. A. Christman.  
Ling, A. R., and D. R. Nanji, ii, 601.  
Lockemann, G., ii, 594.  
Loring, F. H., ii, 570.  
Lottermoser, A., i, 708.  
Lund, Y. See J. E. Greaves.  
Lutz, O., ii, 596.
- McBAIN, J. W., and H. E. Martin,  
ii, 578.  
McBain, J. W., and C. S. Salmon,  
ii, 578.  
Macbeth, A. K., and D. D. Pratt,  
i, 705.  
Macbeth, A. K. See also H. Graham.  
McCann, G. F. See A. F. Hess and  
L. von Moysenbug.  
McCarty, A. C. See R. L. Stähle.  
McCollum, E. V., N. Simmonds,  
P. G. Shipley, and E. A. Park,  
i, 757.  
Mach, F., and F. Sindlinger, ii, 594.  
McLeod, C. M., and G. M. Robinson,  
i, 711.  
Magness, J. R., i, 759.  
Mailhe, A., i, 706.  
Maquenne, L., and R. Cerighelli,  
i, 759.  
Maquenne, L., and E. Demoussy,  
i, 758, 759.  
Marchetti, P. See U. Sborgi.  
Marcusson, J., ii, 590.  
Marsh, J. K. See G. G. Henderson.  
Martin, H. E. See J. W. McBain.  
Martinet, J., i, 732.  
Mauthner, F., i, 726.  
Mayer, A. See M. Samec.

- Meisenheimer, J., and B. Wiegler, i, 739.
- Meissner, K. L. See W. Guertler.
- Meissner, K. W., ii, 565.
- Merkel, P. P. See P. H. M.-P. Brinton.
- Messmer, E. See K. Hess.
- Meyer, H., and A. Hofmann-Meyer, i, 739.
- Meysenbug, L. von, and G. F. McCann, i, 753.
- Meysenbug, L. von, A. M. Pappenheimer, T. F. Zucker, and M. F. Murray, i, 753.
- Middleton, H. E. See C. J. Moore.
- Mirande, M. i, 759.
- Mohler, F. L., and P. D. Foote, ii, 570.
- Moir, J. *TRANS.*, 1654.
- Moore, B. *TRANS.*, 1555.
- Moore, C. J., W. H. Fry, and H. E. Middleton, ii, 608.
- Moore, T. S., i, 742.
- Morgan, G. T., and H. Burgess, *TRANS.*, 1546.
- Morgan, G. T., and W. A. P. Chaljenor, *TRANS.*, 1537.
- Morgulis, S., i, 751.
- Motz, R. See E. Knoevenagel.
- Mouret, (Mlle) and J. Barlot, ii, 597.
- Mügge, O., ii, 576.
- Müller, A., ii, 569.
- Müller, E., and L. Herdergen, i, 741.
- Münch, S., ii, 586.
- Muhlert, F., ii, 594, 595.
- Muhry, G. See O. Skrabal.
- Mukai, G., ii, 593.
- Murakami, T., ii, 589.
- Murayama, Y., and T. Itagaki, i, 760.
- Murray, M. F. See L. von Meysenbug.
- NAKAZONO, T., ii, 596.
- Nanji, D. R. See A. R. Ling.
- Nesti, A. See G. Poma.
- Neumann, B. [with W. Gellenden], ii, 587.
- Neumann, B. [with G. Kotyga], ii, 587.
- Neuschloss, S. M. See H. Bechhold.
- Nieloux, M., ii, 594.
- Noddack, W., ii, 568.
- Nuti, M. See L. Rolla.
- Oye, L. L. See M. R. Jones.
- OLIVERI-MANDALÀ, E., and E. Calderaro, ii, 606.
- Ono, K., i, 726.
- Ost, H., and R. Bretschneider, i, 711.
- Osterberg, A. E., and E. C. Kendall, i, 727.
- Ostwald, W., i, 733.
- PAPPENHEIMER, A. M. See A. F. Hess and L. von Meysenbug.
- Park, E. A. See E. V. McCollum.
- Pascal, P., ii, 574.
- Pascal, P. [with Garnier and Labourasse], ii, 585.
- Passerini, M., i, 743.
- Perkin, W. H., jun., and E. Robinson, i, 706.
- Perkin, W. H., jun., and H. A. Scarborough, i, 728.
- Perkin, W. H., jun. See also W. O. Kermack.
- Perren, E. A. See C. K. Ingold.
- Pfau, A. S., ii, 600.
- Philibert, ii, 605.
- Philippi, E., and F. Auslaender, i, 728.
- Philippi, E., and G. Rie, i, 729.
- Picon, M. See P. Lebeau.
- Pierucci, M., ii, 583.
- Polonovski, M., ii, 601.
- Polonovski, M., and C. Vallée, ii, 593.
- Poma, G., ii, 570.
- Poma, G., and C. Bassi, ii, 571.
- Poma, G., and A. Nesti, ii, 571.
- Pomeranz, H., i, 725.
- Pratolongo, U., ii, 598.
- Pratt, D. D. See A. K. Macbeth.
- RANKE, A. VON, ii, 580.
- Rankine, A. O., ii, 584.
- Räy, (Sir) P. C., and K. Kumar, *TRANS.*, 1643.
- Reclaire, A., ii, 604.
- Réglade, J. See R. Clogne.
- Reilly, A. A. B. See J. N. Collie.
- Reilly, J., and W. J. Hickinbottom, ii, 599.
- Richard, A., ii, 601.
- Rie, G. See E. Philippi.
- Ringer, O. See A. Skrabal.
- Robinson, E. See W. H. Perkin, jun.
- Robinson, G. M. See C. M. McLeod.
- Robinson, R. See W. O. Kermack.
- Rolla, L., and M. Nuti, ii, 597.
- Romani, E. See G. Bruni.
- Rosenblatt, (Mme) M. See G. Bortrand.
- Rosset, H., ii, 598.
- Rudolph, O., ii, 604.
- Rutherford, (Sir) E., ii, 582.
- Ryschkewitsch, E., ii, 586.
- SACCARDI, P., i, 755.
- Salkowski, E., ii, 586.
- Salmon, C. S. See J. W. McBain.
- Samec, M., and A. Mayer, i, 707.
- Sauerland, ii, 595.
- Sborgi, U., and C. Franco, ii, 580.
- Sborgi, U., and P. Marchetti, ii, 572.



- Seaborough, H. A. See W. H. Perkin, jun.  
 Schertz, F. N. See P. H. M. P. Brinton.  
 Schlotz, A. B., ii, 589.  
 Schmidt, G. C., ii, 567.  
 Schmidt, K., ii, 595.  
 Schulek, E., ii, 603.  
 Schweizer, K., i, 757.  
 Seeger, A. See W. Dilthey.  
 Seeliger, R., and D. Thaer, ii, 566.  
 Seidenberg, A., i, 705.  
 Shaffer, P. A., i, 754.  
 Sherwin, C. P., and W. A. Hynes, i, 754.  
 Shipley, P. G. See E. V. McCollum.  
 Short, W. F., i, 749.  
 Simmonds, N. See E. V. McCollum.  
 Simon, O. See W. Dilthey.  
 Simonsen, J. L., TRANS., 1644.  
 Sindlinger, F. See F. Mach.  
 Skrabal, A., and G. Muhry, ii, 581.  
 Skrabal, A., and O. Ringer, ii, 581.  
 Smith, C. R., i, 749.  
 Smith, L., ii, 575.  
 Smith, R. C. See R. Wright.  
 Société Anonyme de Produits Chimiques, i, 706.  
 Société Chimique des Usines du Rhône, i, 737.  
 Society of Chemical Industry in Basle, i, 715, 737.  
 Sörensen, S. P. L., i, 749.  
 Sommerfeld, A., ii, 567.  
 Sordelli, A. See R. Wernicke.  
 Steenhauer, A. J. See L. van Itallie.  
 Stehle, R. L., ii, 605.  
 Stehle, R. L., and A. C. McCarty, i, 755.  
 Steigmann, A., ii, 568.  
 Stevens, H. P., i, 735.  
 Stevenson, H. C. See W. H. Eddy.  
 Stiegler, A., ii, 577.  
 Sugden, S., ii, 576.  
 TAKAGI, S., i, 732.  
 Taucher, R. See W. Dilthey.  
 Thaer, D. See R. Seeliger.  
 Thomas, P., ii, 607.  
 Tisdall, F. F. See B. Kramer.  
 Tomaschek, R., ii, 588.  
 Treichel, O. See W. König.  
 Tröger, J., and A. Berndt, i, 743.  
 Tschirch, A., i, 755.  
 Turner, E. E. See G. J. Burrows.  
 Tutin, F., i, 751.  
 VALLÉE, C. See M. Polonovski.  
 Vaubel, W., ii, 596.  
 WALKER, E. E., TRANS., 1521.  
 Weick, R. See H. Gault.  
 Weissenberger, G., ii, 578.  
 Weitzel, A., ii, 591.  
 Weizmann, C., and D. A. Legg, i, 712.  
 Wernicke, R., and A. Sordelli, i, 758.  
 Wickehorst, H. See W. Borsche.  
 Wiegner, B. See J. Meisenheimer.  
 Wilhelm, R. M., and J. L. Finkelstein, ii, 574.  
 Wiakler, J. See W. Dilthey.  
 Witham, E. See J. Kenner.  
 Wittelsbach, W. See K. Hess.  
 Wood, C. C. See H. R. Le Sueur.  
 Woog, P., ii, 575.  
 Wright, R., and R. C. Smith, TRANS., 1683.  
 YAMAZAKI, E., ii, 574.  
 Yanagisawa, H., i, 760.  
 Yéramian, V., i, 727.  
 Yoder, L. See A. W. Dox.  
 ZUCKER, T. F. See L. von Meysenbug.

## ERRATA.

## VOL. 119 (TRANS., 1921).

Page  
 1339) In equations (6), (7), (8) and in tables II, III, IV for "log<sub>e</sub>"  
 1391) "log<sub>10</sub>"  
 1392)

## VOL. 120 (ABSTR., 1921).

Page Line  
 i, 702 26 for "vitamin-A" read "vitamin-B"

# CONTENTS

## PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY.

	PAGE
CXCIV.— <i>ortho</i> -Chlorodinitrotoluenes. Part IV. 2-Chloro-3:4-dinitrotoluene. By GILBERT T. MORGAN AND THOMAS GLOVER . . . . .	1700
XCXV.—Dinaphtha-1:7:1':7'-diquinone. By GILBERT T. MORGAN and DUDLEY CLOETE VINING . . . . .	1707
CXCVI.—Chenopodium Oil. By THOMAS ANDERSON HENRY and HUMPHREY PAGET . . . . .	1714
CXCVII.— <i>m</i> -Opianic Acid (4:5-Dimethoxy- <i>o</i> -aldehydobenzoic Acid). By ROBERT GEORGE FARGHER and WILLIAM HENRY PERKIN, jun. . . . .	1724
CXCVIII.—The Constitution of Polysaccharides. Part III. The Relationship of <i>l</i> -Glucosan to <i>d</i> -Glucose and to Cellulose. By JAMES COLQUHOUN IRVINE and JOHN WALTER HYDE OLDHAM . . . . .	1744
CXCIX.—Studies in Emulsions. Part III. Further Investigations on the Reversal of Type by Electrolytes. By SHANTI SWARUPA BHATNAGAR . . . . .	1760
CC.—Crystallographic Descriptions of some Pyridine and Picoline Derivatives. By MARY WINEARLS PORTER . . . . .	1769
CCI.—Studies of Halogenohydrins and Related Derivatives in the Cinnamic Acid Series. Part I. By JOHN READ and ALBERTA CATHERINE PRITCHARD ANDREWS . . . . .	1774
CCII.—The Application of Hofmann's Reaction to Substituted Phthalimides. By TOM SIDNEY MOORE, MURIEL TREGARTHEN MARRACK, and ANNIE KATHLEEN PROUD . . . . .	1786
CCIII.— <i>m</i> -Dithiobenzoic Acid. By SAMUEL SMILES and JESSIE STEWART . . . . .	1792
CCIV.—The Rate of Hydrolysis of Methyl Acetate by Hydrochloric Acid in Solutions containing Sucrose. By GEORGE JOSEPH BURROWS . . . . .	1798
CCV.—The Dimorphism of Potassium Ethyl Sulphate. By DALZIEL LLEWELLYN HAMMICK and JOHN MYLNE MULLALLY . . . . .	1802
CVI.—The Friedel-Crafts' Reaction. Part III. Migration of Alkyl Groups in the Benzene Nucleus. By MAURICE COPISAROW . . . . .	1806

	PAGE
CCVII.—Derivatives of 3-Oxy(1)thionaphthen. By SAMUEL SMILES and ERNEST WILSON McCLELLAND . . .	1810
CCVIII.—A New Method for the Resolution of Asymmetric Compounds. By AKIRA SHIMOMURA and JULIUS BEREND COHEN . . .	1816
CCIX.—Derivatives of Tetrahydrocarbazole. By WILLIAM HENRY PERKIN, jun., and SYDNEY GLENN PRESTON PLANT . . .	1825
CCX.—Some Properties of Fused Sodium Hydroxide. By THOMAS WALLACE and ALEXANDER FLECK . . .	1839
CCXI.—Some Derivatives of Monothioethylene Glycol. By GEORGE MACDONALD BENNETT and EDITH MURIEL WHINCOP . . .	1860
CCXII.—Experiments on the Synthesis of the Polyacetic Acids of Methane. Part IV. Conditions of Formation by the Cyanoacetic Ester Method of Stable Methane-triacetic Esters. By CHRISTOPHER KELK INGOLD and EDWARD ARTHUR PERREN . . .	1865
CCXIII.—Experiments on the Synthesis of the Polyacetic Acids of Methane. Part V. The Preparation of Carboxymethanetriacetic Acid. By CHRISTOPHER KELK INGOLD and WALTER JAMES POWELL . . .	1869
CCXIV.—Dichloroacetates and Chlorobromoacetates from $\alpha\beta$ -Dichlorovinyl Ethyl Ether. By HOLLAND CROMPTON and PHYLLIS MARY TRIFFITT . . .	1874
CCXV.—Valency and Co-ordination. By SAMUEL HENRY CLIFFORD BRIGGS . . .	1876
CCXVI.—Studies in the <i>n</i> -Butyl Series. Part I. Aryl <i>n</i> -Propyl Ketones. By GILBERT T. MORGAN and WILFRED JOHN HICKINBOTTOM . . .	1879

## INDEX OF AUTHORS' NAMES

### IN TRANSACTIONS AND ABSTRACTS.

ACKERMANN, D., i, 764	Atkinson, H., ii, 654.
Adams, E. P., ii, 628.	Auwers, K. von, and W. Schaich, i, 806.
Amberger, C., and K. Bromig, i, 833.	BADER, W. See British Cellulose and Chemical Mfg. Co., Ltd.
Anderson, R. J. [with W. L. Kulp], i, 821.	Balz, O. See L. Wöhler.
Andoyer, G., ii, 662.	Bau, A., i, 838.
Andrews, (Miss) A. C. P. See J. Read.	Bauer, H., ii, 657.
Anschütz, R., and A. Hilbert, i, 783.	Baughman, W. F. See G. S. Jamieson.
Ardely, E. See M. Tiffeneau.	Baxter, G. P., ii, 635.
Arndt, F., and E. Milde, i, 813.	
Asahina, Y., and A. Fujita, i, 798.	
Aschan, O., i, 795.	

- Baxter, G. P., and J. H. Hodges, ii, 639.  
 Baxter, G. P., and C. H. Wilson, ii, 640.  
 Becker, R., R. O. Herzog, W. Jancke, and M. Polányi, ii, 627.  
 Benary, E., and M. Schmidt, i, 776.  
 Benedict, S. R., and E. Osterberg, ii, 660.  
 Benirschke, F. See A. Sonn.  
 Bennett, G. M., and (Miss) E. M. Whincop, TRANS., 1860.  
 Bergmann, M., F. Dreyer, and F. Radt, i, 773.  
 Bergmann, M., and A. Miekeley, i, 763.  
 Berner, E., and C. N. Rüber, i, 788.  
 Bernheim, A. See H. Wieland.  
 Bhatnagar, S. S., TRANS., 1760.  
 Biffi, P., ii, 664.  
 Biltz, H., and D. Heidrich, i, 817.  
 Biltz, H., and M. Kobel, i, 815.  
 Birckenbach, L. See O. Hönig-schmid.  
 Blom, A. V., ii, 664.  
 Bodansky, M., ii, 656.  
 Boedecker, F. See J. D. Riedel, Akt. Ges.  
 Böger, O. See W. Schneider.  
 Böhm, P. See H. Wieland.  
 Bolliger, A. See P. Ruggli.  
 Bone, W. A., and W. A. Haward, ii, 628.  
 Borel, C. See A. Jaquerod.  
 Born, M., and W. Gerlach, ii, 632.  
 Bothe, W., and G. Lechner, ii, 617.  
 Boullanger, E., i, 836.  
 Bowen, I. S. See R. A. Millikan.  
 Braecke, (Mlle) M. See M. Bridel.  
 Brand, K., i, 783, 785.  
 Brand, K., and F. Kercher, i, 787.  
 Braun, J. von, and O. Braunsdorf, i, 772.  
 Brauns, D. H. See G. S. Jamieson.  
 Braunsdorf, O. See J. von Braun.  
 Bray, W. C., ii, 629.  
 Brogenzer, A. See E. Knoevenagel.  
 Bridel, M., i, 824.  
 Bridel, M., and (Mlle) M. Braecke, i, 840.  
 Briggs, S. H. C., TRANS., 1876.  
 Briggs, H., ii, 624.  
 Briner, E., ii, 635.  
 British Cellulose and Chemical Mfg. Co., Ltd., W. Bader, and D. A. Nightingale, i, 786.  
 British Dyestuffs Corporation, Ltd., A. G. Green and A. Brittain, i, 805.  
 Brittain, A. See British Dyestuffs Corporation, Ltd.  
 Britton, H. T. S., ii, 657.  
 Broeksmit, T. C. N., ii, 655.  
 Broglie, L. de. See M. de Broglie.  
 Broglie, M. de, and L. de Broglie ii, 615.  
 Bromig, K. See C. Amberger.  
 Brown, E. B. See T. B. Johnson.  
 Browne, C. A., and C. A. Gamble, ii, 661.  
 Bruni, G., and C. Pelizzola, i, 798.  
 Buck, J. S. See I. M. Heilbron.  
 Bullis, D. E. See J. S. Jones.  
 Bullnheimer, ii, 655.  
 Burgess, H. See G. T. Morgan.  
 Burns, R. M. See H. S. Taylor.  
 Burrows, G. J., TRANS., 1798.  
 CAMS, M., i, 821.  
 Campbell, C. See H. B. Dixon.  
 Capps, J. H., ii, 657.  
 Cardini, M., ii, 664.  
 Carpenter, H. C. H., and C. F. Elam, ii, 641.  
 Carter, C. L., i, 833.  
 Challenor, W. A. P. See G. T. Morgan.  
 Chapman, W. R., ii, 629.  
 Ciaccio, C., i, 834.  
 Clemens, C. A., ii, 650.  
 Clinton, G., ii, 618.  
 Cohen, J. B. See A. Shimomura.  
 Cohn, R., ii, 663.  
 Collett, M. E., i, 835.  
 Collie, J. N., and A. A. B. Reilly, i, 800.  
 Copisarow, M. [with C. N. H. Long], TRANS., 1806.  
 Coward, K. H., and J. C. Drummond, i, 837.  
 Crehore, A. C., ii, 632.  
 Cribier, J., ii, 653.  
 Crocker, E. C., i, 839.  
 Crompton, H., and (Miss) P. M. Triffitt, TRANS., 1874.  
 Culbertson, J. B. See W. H. Ross.  
 Curie, M., ii, 616.  
 Cuttat, L. See M. Duboux.  
 Cuy, E. J., ii, 642.  
 DAMIENS, A., ii, 636.  
 Denis, W., and F. B. Talbot, i, 828.  
 Dill, D. B., i, 834.  
 Dixon, H. R., C. Campbell, and A. Parker, ii, 321.  
 Dreyer, F. See M. Bergmann.  
 Drummond, J. C. See K. H. Coward.  
 Duboux, M., and L. Cuttat, i, 763.  
 Dubovitz, H., ii, 639.  
 Duclaux, J., and P. Jeantet, ii, 613.  
 Dunoyer, L., ii, 610.  
 Dutcher, R. A., H. M. Harslaw, and J. S. Hall, i, 839.  
 EBLER, E., and A. J. van Rhyn, ii, 616.  
 Elam, C. F. See H. C. H. Carpenter.  
 Emslander, R. See A. Gutbier.

- Ephraim, F., and E. Michel, ii, 638.  
 Euler, A. C. von, i, 769.
- FAHRION, W., i, 792.  
 Fairbourne, A., i, 794.  
 Fargher, R. G., and W. H. Perkin, jun., TRANS., 1724.  
 Finckh, E. R. O., i, 830.  
 Fleck, A. See T. Wallace.  
 Flintzer, S. See H. Strohmman.  
 François, M., and C. Lormand, ii, 626.  
 Franzen, H., and A. Schneider, ii, 663.  
 Franzen, H., A. Wagner, and A. Schneider, i, 838.  
 Fred, E. B. See W. H. Peterson.  
 Freudenberg, K., and H. Walpuski, i, 799.  
 Freund, E. See E. Speyer.  
 Freund, H. See E. Speyer.  
 Freund, L. See E. Speyer.  
 Freund, W. See E. Speyer.  
 Fricke, K., ii, 659.  
 Fromm, E., and R. Klein, i, 797.  
 Fürth, O., and F. Lieben, i, 820, 828.  
 Fujita, A., i, 792.  
 Fujita, A. See also Y. Asahina.
- GAD-ANDRESEN, K. L., i, 832.  
 Gamble, C. A. See C. A. Browne.  
 Garrison, A. See H. B. Weiser.  
 Gattermann, L., and H. Rolles, i, 817.  
 Gehrcke, E., ii, 612.  
 Gehrcke, E., and L. C. Glaser, ii, 611.  
 Gerlach, W. See M. Born.  
 Gibson, G. E., and W. A. Noyes, ii, 610.  
 Gillet, A., i, 761.  
 Givaudan & Co., L., i, 793.  
 Glaser, L. C. See E. Gehrcke.  
 Glasstone, S., ii, 640.  
 Glatfielder, A. See P. Karrer.  
 Glover, T. See G. T. Morgan.  
 Gossner, B., ii, 649.  
 Gramont, A. de, and G. A. Hemsalech, ii, 611.  
 Green, A. See British Dyestuffs Corporation, Ltd.  
 Grothsch, V. E., and W. C. Smith, ii, 659.  
 Grün, A., and T. Wirtz, ii, 660.  
 Günther-Schulze, A., ii, 624, 642.  
 Guertler, W., and K. L. Meissner, ii, 640.  
 Gutbier, A., and R. Emslander, ii, 636.
- HAAS, P., i, 839.  
 Hackh, I. W. D., i, 800.  
 Haenseler, C. M., i, 836.  
 Hagen, O., ii, 634.  
 Hahn, F., ii, 634.
- Halberkann, J., i, 779.  
 Hall, C. H., jun., ii, 651.  
 Hall, J. S. See R. A. Dutcher.  
 Hamnick, D. L., and J. M. Mullaly, TRANS., 1802.  
 Harshaw, H. M. See R. A. Dutcher.  
 Hart, E. B., H. Steenbock, and C. A. Hoppert, i, 829.  
 Hasselskog, S., ii, 651.  
 Haughton, J. L., ii, 641.  
 Hauser, E., and E. Rie, ii, 623.  
 Haward, W. A. See W. A. Bone.  
 Heidrich, D. See H. Biltz.  
 Heiduschka, A., and A. Steinruck, i, 833.  
 Heilbron, I. M., and J. S. Buck, i, 793.  
 Hein, F., i, 826.  
 Heise, F. See K. W. Rosenmund.  
 Helwig, E. L., ii, 653.  
 Hemsalech, G. A. See A. de Gramont.  
 Henderson, G. G., and J. K. Marsh, i, 797.  
 Henderson, G. H., ii, 617.  
 Hendrixson, W. S., ii, 651.  
 Henrich, F., ii, 617.  
 Henry, T. A., and H. Paget, TRANS., 1714.  
 Herzog, R. O. See R. Becker.  
 Hess, K., and H. Rheinboldt, i, 777.  
 Hickinbottom, W. J. See G. T. Morgan.  
 Hilbert, A. See R. Anschütz.  
 Hintikka, S. V., i, 772.  
 Hjort, A. M., and C. E. Kaufmann, i, 834.  
 Hodges, J. H. See G. P. Baxter.  
 Höngschmid, O., and L. Birckenbach, ii, 646.  
 Hoover, C. R., ii, 654.  
 Hopff, H. See K. H. Meyer.  
 Hoppert, C. A. See E. B. Hart.  
 Horsch, W. G. See R. E. Wilson.  
 Horton, E., ii, 661.  
 Hulot, P., ii, 656.  
 Hurwitz, O. See P. Karrer.
- INGOLD, C. K., and E. A. Perren, TRANS., 1865; i, 763.  
 Ingold, C. K., and W. J. Powell, TRANS., 1869.  
 Irvine, J. C., and J. W. H. Oldham, TRANS., 1744.  
 Isgarischev, N., ii, 620.  
 Ishiwara, T., ii, 643.
- JACOB, W., i, 794.  
 Jäger, O. See E. Knoevenagel.  
 Jamieson, G. S., W. F. Baughman, and D. H. Brauns, i, 840.  
 Jancke, W. See R. Becker.  
 Jaquero, A., and C. Borel, ii, 635.

- Jassoy, H. See A. Sieglitz.  
 Jeantet, P. See J. Duclaux.  
 Johnson, T. B., and E. B. Brown, i, 806.  
 Jones, J. S., and D. E. Bullis, i, 840.  
 Jones, L. H., and J. W. Shive, i, 838.
- KARRER, P., i, 765, 801.  
 Karrer, P., and O. Hurwitz, i, 767.  
 Karrer, P., C. Nägeli, O. Hurwitz, and A. Wälti, i, 768.  
 Karrer, P., and S. Rosenfeld, i, 793.  
 Karrer, P., A. Rüdinger, A. Glattfelder, and L. Waitz, A., i, 800.  
 Karrer, P., and A. P. Smirnov, i, 766.  
 Karrer, P., and F. Widmer, i, 771.  
 Karrer, P., F. Widmer, and A. P. Smirnov, i, 765.  
 Kaufmann, C. E. See A. M. Hjort.  
 Kauko, Y., i, 771.  
 Kelber, C., ii, 630.  
 Kemble, E. C., ii, 632.  
 Kercher, F. See K. Brand.  
 Kermack, W. O., W. H. Perkin, jun., and R. Robinson, i, 802.  
 Keys, D. A., ii, 628.  
 King, A. S., ii, 610, 612.  
 Kingsbury, F. B., and W. W. Swanson, ii, 662.  
 Klason, P., i, 840.  
 Klein, R. See E. Fromm.  
 Knoevenagel, E. [with O. Jäger], i, 785.  
 Knoevenagel, E., and A. Bregenzner, i, 771.  
 Kobel, M. See H. Biltz.  
 Köhler, A. See W. Schneider.  
 Kohnschütter, V., and H. Stäger, ii, 619.  
 Kondó, K., i, 840.  
 Konrad, E. See R. Schwarz.  
 Kozłowski, A., i, 840.  
 Kramer, B. See F. F. Tisdall.  
 Krasinska, Z. See J. K. Parnas.  
 Krause, E. [with G. S. Reissaus], i, 825.  
 Kulp, W. L. See R. J. Anderson.  
 Kumar, K. See (Sir) P. C. Rây.
- LAAR, J. J. van, ii, 622.  
 Labbé, H., and G. de Toni, ii, 655.  
 Labes, R., i, 820.  
 Laing, M. E., ii, 628.  
 Langelius, E. W. See S. Odén.  
 Larmor, (Sir) J., ii, 632.  
 Laska-Mintz, E. See J. K. Parnas.  
 Lassieur, A., ii, 651.  
 Laue, M. von, ii, 626.  
 Lechner, G. See W. Bothe.  
 Le Grand, L., ii, 661.  
 Le Sueur, H. R., and C. C. Wood, i, 792.
- Levene, P. A., i, 821; ii, 613.  
 Lévy, (Mlle) J., i, 788.  
 Lewandowski, M. See E. Waser.  
 Lewis, W. C. M., and A. McKeown, ii, 623.  
 Lieben, F. See O. Fürth.  
 Lizius, J. L., ii, 650.  
 Loch, J., i, 819, 822.  
 Long, C. N. H. See M. Copisarow.  
 Lormand, C. See M. François.  
 Ludwig, R. See E. Weitz.  
 Lumière, A., L. Lumière, and A. Seyewetz, ii, 615.  
 Lumière, L. See A. Lumière.
- MAASS, O., and J. Russell, i, 761.  
 McClelland, E. W. See S. Smiles.  
 McClendon, J. F., i, 839.  
 MacInnes, D. A., ii, 619.  
 McKeown, A. See W. C. M. Lewis.  
 Madelung, W., i, 810.  
 Mallemann, D. de, ii, 614.  
 Marrack, (Miss) M. T. See T. S. Moore.  
 Marsh, J. K. See G. G. Henderson.  
 Masing, G., ii, 639.  
 Matejka, J., ii, 658.  
 Mathieu, L., ii, 662.  
 Matsubara, A., ii, 644.  
 Matsuno, K., ii, 637, 644.  
 Mattaar, T. J. F. See J. Timmermans.  
 Meissner, K. L. See W. Guertler.  
 Menzies, A. W. C., ii, 622.  
 Menzies, A. W. C., and S. L. Wright, ii, 622.  
 Merton, T. R., ii, 611.  
 Meyer, K. H., and H. Hopff, i, 776.  
 Meyer, K. H., and L. Orthner, i, 775.  
 Michel, E. See F. Ephraim.  
 Miekeley, A. See M. Bergmann.  
 Milbauer, J., and J. Pazourek, ii, 635.  
 Milde, E. See F. Arndt.  
 Millikan, R. A., I. S. Bowen, and R. A. Sawyer, ii, 609.  
 Mitchell, P. H., and J. W. Wilson, i, 830.  
 Moir, J., ii, 613.  
 Monier-Williams, G. W., ii, 650.  
 Moore, B., i, 829.  
 Moore, T. S., (Miss) M. T. Marrack, and (Miss) A. K. Proud, TRANS., 1786.  
 Morgan, G. T., and H. Burgess, i, 817.  
 Morgan, G. T., and W. A. P. Challenor, i, 808.  
 Morgan, G. T., and T. Glover, TRANS., 1700.  
 Morgan, G. T., and W. J. Hickinbottom, TRANS., 1879.  
 Morgan, G. T., and D. C. Vining, TRANS., 1707.

- Müller, R., i, 830.  
 Mullaly, J. M. See D. L. Hammick.  
 Murschhauser, H., i, 765.  
 Myers, V. C., and J. J. Short, i, 828.
- NAGELI, C. See P. Karrer.  
 Nagayama, T., i, 836.  
 Nelken, A. See E. Weitz.  
 Nightingale, D. A. See British Cellulose and Chemical Mfg. Co., Ltd.  
 Northrop, J. H., i, 823.  
 Noyes, W. A. See G. E. Gibson.
- ODÉN, S., and E. W. Langelius, ii, 625.  
 Oldham, J. W. H. See J. C. Irvine.  
 Orékhoff, A. See M. Tiffeneau.  
 Orthner, L. See K. H. Meyer.  
 Osterberg, E. See S. R. Benedict.
- PAGET, H. See T. A. Henry.  
 Parker, A. See H. B. Dixon.  
 Parnas, J. K., i, 831, 832.  
 Parnas, J. K., and Z. Krasinska, i, 833.  
 Parnas, J. K., and E. Laska-Mintz, i, 831.  
 Parsons, J. P. See W. H. Ross.  
 Partington, J. R., ii, 621.  
 Paschke, F., i, 772.  
 Pazourek, J. See J. Milbauer.  
 Pelizzola, C. See G. Bruni.  
 Perkin, W. H., jun., and S. G. P. Plant, TRANS., 1825.  
 Perkin, W. H., jun. See also R. G. Fargher and W. O. Kermack.  
 Perren, E. A. See C. K. Ingold.  
 Peterson, W. H., E. B. Fred, and J. H. Verhulst, i, 836.  
 Phillips, M., i, 811.  
 Pictet, A., and J. Pictet, i, 766.  
 Pictet, J. See A. Pictet.  
 Plant, S. G. P. See W. H. Perkin, jun.  
 Plauson, H., ii, 627.  
 Plausons Forschungsinstitut, G. m. b. H., i, 762.  
 Polányi, M. See R. Becker.  
 Porter, (Miss) M. W., TRANS., 1769.  
 Powell, W. J. See C. K. Ingold.  
 Pringsheim, J., ii, 612.  
 Froud (Miss), A. K. See T. S. Moore.
- QUAGLIARIELLO, G., i, 831.
- RACKE, F. See R. Willstätter.  
 Radt, F. See M. Bergmann.  
 Rahn, F. See H. Wieland.  
 Rast, K., ii, 623.  
 Ray, (Sir) P. C., and K. Kumar, i, 762.  
 Read, J., and (Miss) A. C. P. Andrews, TRANS., 1774.  
 Reilly, A. A. B. See J. N. Collic.
- Reindel, F. See H. Wieland.  
 Reinkober, O., ii, 613.  
 Reisenegger, C. See H. Wieland.  
 Reissaus, G. S. See E. Krause.  
 Roychler, A., i, 768.  
 Rheinboldt, H. See K. Hess.  
 Rhyn, A. J. van. See E. Ebler.  
 Ricker, N. H., ii, 609.  
 Rie, E. See E. Hauser.  
 Riedel, J. D., Akt. Ges., i, 774, 825.  
 Riedel, J. D., Akt. Ges., and F. Boedeker, i, 774.  
 Riiber, C. N. See E. Berner.  
 Rinne, F., ii, 626.  
 Robinson, R. See W. O. Kermack.  
 Rolfes, H. See L. Gattermann.  
 Rosenfold, S. See P. Karrer.  
 Rosenmund, K. W., and F. Zetzsche, ii, 631.  
 Rosenmund, K. W., F. Zetzsche, and F. Heise, ii, 631.  
 Rosenthal, B. See A. Schönberg.  
 Ross, W. H., J. B. Culbertson, and J. P. Parsons, i, 761.  
 Roth, A. See E. Weitz.  
 Roure-Bertrand Fils, i, 797, 798.  
 Rüdinger, A. See P. Karrer.  
 Ruggli, P., and A. Bolliger, i, 811, 812.  
 Russell, J. See O. Maass.  
 Ruzicka, L., and H. Trebler, i, 796.
- SACHS, G., i, 762.  
 Sasaki, T., i, 808.  
 Sawyer, R. A. See R. A. Millikan.  
 Schaal, R. B., ii, 659.  
 Schaich, W. See K. von Auwers.  
 Schatzkes, J. See A. Sieglitz.  
 Schlötter, M., ii, 620.  
 Schmidt, H., i, 775.  
 Schmidt, M. See E. Benary.  
 Schneider, A. See H. Franzen.  
 Schneider, W., and O. Böger, i, 801.  
 Schneider, W., and A. Köhler, i, 803.  
 Schönberg, A., and B. Rosenthal, i, 808.  
 Schoep, A., ii, 649.  
 Schwarz, R., and E. Konrad, ii, 645.  
 Schwarz, R., and H. Stock, ii, 614.  
 Seyewetz, A. See A. Lumière.  
 Shumomura, A., and J. B. Cohen, TRANS., 1816.  
 Shive, J. W. See L. H. Jones.  
 Short, J. J. See V. C. Myers.  
 Sieglitz, A., and H. Jassoy, i, 791.  
 Sieglitz, A., and J. Schatzkes, i, 781, 792.  
 Simonsen, J. L., i, 797.  
 Slyke, D. D. van, i, 828.  
 Smekal, A., ii, 615.  
 Smiles, S., and E. W. McClelland, TRANS., 1810.  
 Smiles, S., and (Miss) J. Stewart, TRANS., 1792.

- Smirnov, A. P., i, 812.  
 Smirnov, A. P. See also P. Karrer.  
 Smith, J. H., ii, 652.  
 Smith, R. C. See R. Wright.  
 Smith, W. C. See V. E. Grotlisch.  
 Snapper, I., i, 834.  
 Snoo, K. de, i, 828.  
 Sondal, J. A., ii, 654.  
 Sonn, A., and F. Benirschke, i, 805.  
 Speyer, E., E. Freund, W. Freund,  
 H. Freund, and L. Freund, i, 803.  
 Stäger, H. See V. Kohlschütter.  
 Stahrross, K., i, 794.  
 Steenbock, H. See E. B. Hart.  
 Steinruck, A. See A. Heiduschka.  
 Stewart, (Miss) J. See S. Smiles.  
 Stock, H. See R. Schwarz.  
 Strohmman, H., and S. Flintzer,  
 ii, 664.  
 Swanson, W. W. See F. B. Kings-  
 bury.  
 TAKAHASHI, E., i, 832.  
 Talbot, F. B. See W. Denis.  
 Tammann, G., ii, 647.  
 Taylor, H. S., and R. M. Burns,  
 ii, 630.  
 Terroine, E. F., and R. Wurmser,  
 i, 837.  
 Tiffeneau, M., and E. Ardely, i, 775.  
 Tiffeneau, M., and A. Orékhoft,  
 i, 788.  
 Timmermans, J., and T. J. F.  
 Matthaar, ii, 622.  
 Tisdall, F. F., and B. Kramer, ii, 655.  
 Tomita, M., i, 829, 830, 834.  
 Toni, G. de. See H. Labbé.  
 Trebler, H. See L. Ruzicka.  
 Triffitt, (Miss) P. M. See H. Crompton.  
 True, R. H., i, 837.  
 Twitchell, E., ii, 662.  
 UKE, H. W. van, ii, 660.  
 VEGARD, L., ii, 627.  
 Velich, V., ii, 658.  
 Verhulst, J. H. See W. H. Peterson.  
 Vining, D. C. See G. T. Morgan.  
 WALTI, A. See P. Karrer.  
 Wagenmann, K., ii, 658.  
 Wagner, A. See H. Franzen.  
 Waitz, L. See P. Karrer.  
 Walker, E. E., ii, 624.  
 Wallace, T., and A. Fleck, TRANS.,  
 i, 1839.  
 Walpuski, H. See K. Freudenberg.  
 Waser, E., and M. Lewandowski,  
 i, 788.  
 Watanabe, K. See E. Yoshitomi.  
 Weber, H. C. P., ii, 645.  
 Weinberg, A. von, i, 778, 781.  
 Weiser, H. B., ii, 625.  
 Weiser, H. B., and A. Garrison,  
 ii, 637.  
 Weitz, E., and A. Nelken [with R.  
 Ludwig], i, 804.  
 Weitz, E., A. Roth, and A. Nelken,  
 i, 804.  
 Wesson, L. G., i, 796.  
 Whincop, (Miss) E. M. See G. M.  
 Bennett.  
 Wichers, E., ii, 648.  
 Widmer, F. See P. Karrer.  
 Wieland, H., i, 802.  
 Wieland, H. [with A. Bernheim,  
 P. Böhm, and C. Reisenegger],  
 i, 778.  
 Wieland, H., and F. Rahn [with  
 F. Reindel], i, 782.  
 Willstätter, R., and F. Racke, i, 823.  
 Wilson, C. H. See G. P. Baxter.  
 Wilson, J. W. See P. H. Mitchell.  
 Wilson, R. E., W. G. Horsch, and  
 M. A. Youtz, ii, 643.  
 Winkler, J. W., ii, 656.  
 Wirth, T., ii, 651.  
 Wirth, T. See also A. Grün.  
 Wöhler, L., and O. Balz, ii, 633.  
 Wood, C. C. See H. R. Le Sueur.  
 Wright, R., and R. C. Smith,  
 ii, 630.  
 Wright, S. L. See A. W. C. Menzies.  
 Wurschmidt, J., ii, 646.  
 Wurmser, R. See E. F. Terroine.  
 Wuth, O., i, 835.  
 YOSHITOMI, E., and K. Watanabe,  
 i, 775.  
 Youtz, M. A. See R. E. Wilson.  
 ZETZSCHE, F. See K. W. Rosen-  
 mund.



## ERRATA.

VOL. 120 (ABSTR., 1921).

Page	Line	
i, 751	8	for "twice" read "half."
ii, 285	14*	"Thompson" read "Thomson."
ii, 285	9*	"Thompson" "Thomson."

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\* From bottom.

# CONTENTS

## PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY.

	PAGE
CCXVII.—The Nitro- and Amino-derivatives of 4-Phenyl-glyoxaline. By REGINALD LINDSAY GRANT and FRANK LEE PYMAN . . . . .	1893
CCXVIII.—The Explosion of Acetylene and Nitrogen. Part I. By WILLIAM EDWARD GARNER and KICHIMATSU MATSUNO . . . . .	1903
CCXIX.—Physical Chemistry of the Oxides of Lead. Part II. The Supposed Enantiotropy of Lead Monoxide. By SAMUEL GLASSTONE . . . . .	1914
CCXX.—Investigations into the Analytical Chemistry of Tantalum, Columbium, and their Mineral Associates. I. The Use of Tartaric Acid in the Analysis of Natural Tantolocolumbates. II. The Separation of Zirconium from Tantalum and from Columbium. By WALTER RAYMOND SCHOELLER and ALAN RICHARD POWELL . . . . .	1927
CCXXI.—Catalysis of the Mutarotation of Dextrose by Metals. By WILLIAM EDWARD GARNER and DOUGLAS NORMAN JACKMAN . . . . .	1936
CCXXII.—The Decomposition of Ozone by Light of the Visible Spectrum. By ROBERT OWEN GRIFFITH and WILLIAM JAMES SHUTT . . . . .	1948
CCXXIII.—Syntheses in the Thianthren Series. Part I. By JÑANENDRA NATH RÂY . . . . .	1959
CCXXIV.—The Solubility of Glucinum Sulphate in Water and Sulphuric Acid at 25°. By HUBERT THOMAS STANLEY BRITTON . . . . .	1967
CCXXV.—Studies on the Dependence of Optical Rotatory Power on Chemical Constitution. Part IV. Aryl Derivatives of Bisiminocamphor. By BAWA KARTAR SINGH, MAHAN SINGH, and JIWAN LAL . . . . .	1971
CCXXVI.—The Reversibility of the Michael Reaction. By CHRISTOPHER KELK INGOLD and WALTER JAMES POWELL . . . . .	1976
CCXXVII.—Complex Metallic Ammines. Part VI. <i>cis</i> -Phthalato-, <i>cis</i> -Homophthalato-, and other Diethylene-diaminecobaltic Salts. By JAMES COOPER DUFF . . . . .	1982

	PAGE
CCXXXVIII.—The Separation of Miscible Liquids by Distillation. By ARTHUR FELIX DUFTON . . . . .	1988
CCXXXIX.—The Colour of Iron Alum. By JANE BONNELL and EDGAR PHILIP PERMAN . . . . .	1994
CCXXX.—The Direct Iodometric Estimation of Lead Peroxide. By SAMUEL GLASSTONE . . . . .	1997
CCXXXI.—The Conditions Underlying the Formation of Unsaturated and Cyclic Compounds from Halogenated Open-chain Derivatives. Part III. Products derived from Halogenated Glutaconic Acids. By ERNEST HAROLD FARMER and CHRISTOPHER KELK INGOLD . . . . .	2001
CCXXXII.—Studies in the Dihydronaphthalene Series. Part II. The <i>ar</i> -Dihydro- $\alpha$ -naphthols and their Derivatives. By FREDERICK MAURICE ROWE and ESTHER LEVIN . . . . .	2021
CCXXXIII.—Researches on Sulphuryl Chloride. Part I. Influence of Catalysts: a Convenient Method of Chlorinating Benzene. By OSWALD SILBERRAD . . . . .	2029
CCXXXIV.—The Adsorption of Thorium- <i>B</i> and Thorium- <i>C</i> by Ferric Hydroxide. By JOHN ARNOLD CRANSTON and ROBERT ALEXANDER BURNETT . . . . .	2036
CCXXXV.—Metallic Derivatives of Nitrophenolic Compounds. Part II. Some Nitrotoloxides of Metals of Group II. By DOROTHY GODDARD and ARCHIBALD EDWIN GODDARD . . . . .	2044
CCXXXVI.—The Reaction between Persulphates and Silver. By GEOFFREY ISHERWOOD HIGSON . . . . .	2048
CCXXXVII.—Structure and Colour of the Azine Scarlet. By JULIUS BEREND COWEN and HERBERT GRACE CRABTREE . . . . .	2055
CCXXXVIII.—The Action of Light of Short Wave-lengths on some Organic Acids and their Salts. By FRANS MAURITS JAEGER . . . . .	2070
CCXXXIX.—A New Synthesis of Oxazines. By ARTHUR FAIRBOURNE and HAROLD TOMS . . . . .	2076
CXCL.—The Influence of Neutral Salts on the Hydrolysis of Ethyl Formate. By ALEXANDER BERNARD MANNING . . . . .	2079
CXCLI.—The Action of Diazo-salts on Aromatic Sulphonamides. Part I. By PAVITRA KUMAR DUTT, HUGH ROBINSON WHITEHEAD, and ARTHUR WORMALL . . . . .	2088
CCXLII.—The Optically Active Forms of the Keto-dilactone of Benzophenone-2:4:2':4'-tetracarboxylic Acid. By WILLIAM HOBSON MILLS and CHARLES REYNOLDS NODDER . . . . .	2094
CCXLIII.—Production of Picric Acid from the Sulphonic Acids of Phenol. By RUTH KING . . . . .	2105
OBITUARY NOTICES . . . . .	2120

## INDEX OF AUTHORS' NAMES

## IN TRANSACTIONS AND ABSTRACTS.

- ADOLF, M., and W. Pauli, ii, 700.  
 Albrecht, E., ii, 675.  
 Andoyer, G., ii, 704.  
 Andrews, A. C. P. See J. Read.  
 Anselm, F. See K. Hess.  
 Arndt, F. [with E. Milde and G. Eckert], i, 842.  
 Attack, F. W., and G. W. Clough, i, 870.  
 Auerbach, R., ii, 680.  
 BACKER, H. J., i, 855.  
 Bailey, G. H., and F. Boettner, i, 879.  
 Balareff, D., ii, 708, 712.  
 Bargellini, G., and C. Moneada, i, 865.  
 Barnett, W. L., i, 847.  
 Barthélemy, H. See E. F. Terroine.  
 Baru, R. See B. M. Margosches.  
 Bell, H. See W. L. Bragg.  
 Bennett, C. T., ii, 717.  
 Bennett, G. M., and E. M. Whincop, i, 842.  
 Berl, E., and W. von Boltenstern, ii, 705.  
 Berthelot, A., and (Mlle) E. Ossart, i, 909.  
 Bertrand, G., and R. Vladesco, i, 907.  
 Bhatnagar, S. S., ii, 685.  
 Biltz, H., and F. Max, i, 893, 895.  
 Biltz, H., and R. Robl, i, 891, 893.  
 Birge, R. T., ii, 666.  
 Blaszkowskie, H. i Z. See W. Swientoslawski.  
 Blau, N. F., ii, 718.  
 Bodansky, M., i, 907.  
 Bodecker, F., and H. Volk, i, 865.  
 Böeseken, J., i, 843, 844.  
 Böeseken, J., and B. B. C. Felix, i, 844.  
 Böeseken, J., and (Mlle) P. Ouwehand, i, 861.  
 Boettner, F. See G. C. Bailey.  
 Boltenstern, W. von. See E. Berl.  
 Bonnell, J., and E. P. Ferman, TRANS., 1994.  
 Borsche, W., and A. Roth, i, 862.  
 Bouillot, J., i, 884.  
 Bowman, S., ii, 706.  
 Bragg, W. L., and H. Bell, ii, 689.  
 Brauner, B., ii, 691.  
 Briggs, S. H. C., ii, 691.  
 British Dyestuffs Corporation, Ltd., A. G. Green, and D. A. Clibbens, i, 853.  
 British Dyestuffs Corporation, Ltd., A. G. Green, and A. E. Herbert, i, 854.  
 Britton, H. T. S., TRANS., 1967; ii, 712.  
 Brown, J. G., ii, 676.  
 Brown, S. M. See W. P. Kelley.  
 Bruhns, G., ii, 705.  
 Bürker, K., ii, 720.  
 Burnett, R. A. See J. A. Cranston.  
 Burrows, G. J., ii, 688.  
 CAPPENBERG, H., ii, 720.  
 Chadwick, J. See (Sir) E. Rutherford.  
 Charpy, G., and G. Decorps, ii, 709.  
 Chatterji, N. G., ii, 713.  
 Chemische Fabrik Rhenania Akt.-Ges., B. C. Stuer, and W. Grob, i, 852.  
 Christensen, H. R., and N. Feilberg, ii, 711.  
 Clarens, J., ii, 719.  
 Claude, G., ii, 692.  
 Clibbens, D. A. See British Dyestuffs Corporation, Ltd.  
 Clough, G. W. See F. W. Attack.  
 Coffignier, C. See P. Nicolardot.  
 Cohen, J. B., and H. G. Crabtree, TRANS., 2055.  
 Cohen, J. B. See also A. Shimomura.  
 Copaux, H., ii, 707.  
 Copisarow, M. [with C. N. H. Long], i, 853.  
 Crabtree, H. G. See J. B. Cohen.  
 Cranston, J. A., and R. A. Burnett, TRANS., 2036.  
 Crittenden, E. C. See E. B. Rosa.  
 Crompton, H., and P. M. Trifitt, i, 842.  
 Crowther, J. A., ii, 673.  
 DAS, A. K., and B. N. Ghosh, i, 896.  
 Dauvillier, A., ii, 669.  
 David, W. T., ii, 687.  
 Davies, A. C. See F. Horton.  
 Décombe, ii, 676.  
 Decorps, G. See G. Charpy.  
 Devrient, W., i, 909.  
 Dieckmann, W., ii, 716.  
 Dingle, H., ii, 668.  
 Dorsey, N. E., ii, 675.  
 Dubosc, A., ii, 718.  
 Duff, J. C., TRANS., 1982.

- Dufton, A. F., *TRANS.*, 1988.  
 Dutt, P. K., H. R. Whitehead, and A. Wormall, *TRANS.*, 2088.
- EAKLE, A. S., ii, 702.  
 Eckert, A., i, 854, 870.  
 Eckert, A., and G. Endler, i, 871.  
 Eckert, A., and F. Seidel, i, 862.  
 Eckert, G. See F. Arndt.  
 Eddy, N. B., i, 906.  
 Ege, R., and V. Henriques, i, 905.  
 Eggert, J., and B. Scharnow, ii, 686, 691.  
 Ehn, M. See W. C. Thro.  
 Elbs, K., and P. Neher, ii, 693.  
 Elliott, F. A., and S. E. Sheppard, ii, 720.  
 Endler, G. See A. Eckert.  
 Engeland, R., i, 880.  
 Euler, A. C. von, i, 849.  
 Evans, C. L., i, 904.  
 Evers, F. See C. Harries.  
 Evers, N., ii, 705.
- FAIRBOURNE, A., and H. Toms, *TRANS.*, 2076.  
 Falcicola, P., ii, 711.  
 Fargher, R. G., and W. H. Perkin, jun., i, 865.  
 Farmer, E. H., and C. K. Ingold, *TRANS.*, 2001.  
 Følberg, N. See H. R. Christensen.  
 Felix, B. B. C. See J. Böcsken.  
 Felix, W. See K. H. Meyer.  
 Fischer, A. von, i, 848.  
 Fleck, A. See T. Wallace.  
 Fleischer, K., ii, 714.  
 Florentin, D., ii, 707.  
 Flury, F. See A. Gutbier.  
 Fournier, L., and L. Guénot, i, 908.  
 Friend, J. N., ii, 678.  
 Fulmer, E. I., i, 910.  
 Funcke, S., i, 907.
- GARNER, W. E., and D. N. Jackman, *TRANS.*, 1936.  
 Garner, W. E., and K. Matsuno, *TRANS.*, 1903.  
 Garrison, A. See H. B. Weiser.  
 Geijer, P., ii, 702.  
 Ghosh, B. N. See A. K. Das.  
 Giua, Mario. See Michele Giua.  
 Giua, Michele, and Mario Giua, i, 858.  
 Glasstone, S., *TRANS.*, 1914, 1997.  
 Glover, T. See G. T. Morgan.  
 Glud, W., ii, 697.  
 Goddard, A. E. See D. Goddard.  
 Goddard, D., and A. E. Goddard, *TRANS.*, 2044.  
 Goebel, A. See H. Lecher.  
 Grandmougin, E., i, 871, 889.  
 Grant, R. L., and F. L. Pyman, *TRANS.*, 1893.
- Graumann, E. See E. Schmidt.  
 Green, A. G. See British Dyestuffs Corporation, Ltd.  
 Griffith, R. O., and W. J. Shutt, *TRANS.*, 1948.  
 Grimme, C., ii, 720.  
 Grob, W. See Chemische Fabrik Rhenania Akt.-Ges.  
 Guénot, L. See L. Fournier.  
 Gutbier, A., and F. Flury [with F. Heinrich], ii, 693.
- HAAG, J. R. See A. G. McCall.  
 Haar, A. W. van der, i, 877.  
 Iachl, A. See J. Martinet.  
 Hähle, H. See R. Scholl.  
 Haendel, L., and K. W. Joetten, i, 908.  
 Hagenböcker, A. See M. P. Schmidt.  
 Hahn, F. V. von, ii, 684.  
 Haldane, J. B. S., i, 904.  
 Haller, A., and (Mine) P. Ramart, i, 874.  
 Hallimond, A. F. [with J. H. Whiteley], ii, 702.  
 Hammett, F. S., i, 906.  
 Hammick, D. L., and J. M. Mullaly, i, 841.  
 Hance, F. E. See F. H. Rhodes.  
 Hannik, M., ii, 685.  
 Harkins, W. D., ii, 690.  
 Harries, C., and F. Evers, ii, 698.  
 Harrop, G. A., jun., ii, 715.  
 Heering, H. See H. Leuchs.  
 Heinrich, F. See A. Gutbier.  
 Heller, G., i, 891.  
 Hellriegel, E. See H. Leuchs.  
 Henrich, F. [with N. Matulka, G. Opfermann, K. Roedel, F. Rossteutscher, and W. Wunder], i, 886.  
 Henriques, V. See R. Ege.  
 Henry, T. A., and H. Paget, i, 874.  
 Hepburn, N. W., ii, 716.  
 Herbert, A. E. See British Dyestuffs Corporation, Ltd.  
 Herz, W., ii, 678.  
 Hess, K., and F. Anselm, i, 881.  
 Heuser, C., and A. Winsvold, i, 845.  
 Heuser, E., and G. Wenzel, ii, 715.  
 Hewlett, C. W., ii, 674.  
 Hickinbottom, W. J. See G. T. Morgan.  
 Hiedemann, E., ii, 694.  
 Higson, G. I., *TRANS.*, 2048.  
 Hoffmann, H., ii, 677.  
 Holde, D., and I. Tacke, i, 842.  
 Holmberg, B., i, 849.  
 Holmberg, B., and M. Sjöberg, i, 850.  
 Holmberg, B., and T. Wintzell, i, 850.  
 Honda, K., and T. Murakami, ii, 699.

- Hopff, H. See K. H. Meyer.  
 Iorton, F., and A. C. Davies, ii, 672.  
 Hughes, W. E., ii, 677.  
 Hutchinson, A., and A. M. Macgregor, ii, 701.  
 Gl, S., i, 841.  
 Kawa, M., ii, 706.  
 ngold, C. K., and E. A. Perren, i, 845.  
 ngold, C. K., and W. J. Powell, TRANS., 1976; i, 845.  
 ngold, C. K. See also E. H. Farmer.  
 rvine, J. C., and J. W. H. Oldham, i, 846.  
 ACKMAN, D. N. See W. E. Garner.  
 agor, F. M., TRANS., 2070.  
 änecke, E., ii, 697.  
 ander, G., and H. C. Stuhlmann, ii, 711.  
 encks, Z., i, 913.  
 ilek, A., ii, 712.  
 oetten, K. W. See L. Haendel.  
 ones, F. R., i, 914.  
 ones, G., and W. C. Schumb, ii, 676.  
 orissen, W. P., ii, 688.  
 ĀDLCOVÁ, (Mlle) A., ii, 680.  
 ameiyama, N., ii, 697.  
 anó, N., ii, 718.  
 eitholtz, A., ii, 708.  
 elber, C., ii, 688.  
 eller, R., ii, 682.  
 elley, W. P., and S. M. Brown, ii, 915.  
 empf, N., i, 915.  
 ern, E. J. See J. A. Wilson.  
 ing, R., TRANS., 2105.  
 lein, P., ii, 684.  
 lein, P. See also I. Traube.  
 lemenc, A., ii, 692.  
 noovenagel, E., and G. Oelbermann, i, 865.  
 Kohen, W., ii, 710.  
 Kohlweiler, E., ii, 689.  
 Koller, P., ii, 701.  
 Kolthoff, I. M., ii, 705, 711, 713.  
 Kondó, H., and S. Saio, i, 882.  
 Kornfeld, G., ii, 670.  
 Kreis, H., and J. Studinger, i, 905.  
 Kroll, S. See C. Mannich.  
 Kunau, F. See W. Schneider.  
 LAL, J. See B. K. Singh.  
 La Porte, N. M., ii, 699.  
 Landé, A., ii, 669.  
 Langmuir, I., ii, 689.  
 Lassieur, A., and (Mme) A. Lassieur, ii, 712.  
 Lassieur, (Mme) A. See A. Lassieur.  
 Lautenschläger, L., i, 907.  
 Lecher, H., and A. Goebel, i, 853.  
 Lecher, H., and K. Simon, i, 860.  
 Lederle, P. See F. Mach.  
 Lehmann, R. See A. Lottermoser.  
 Lepierre, C., ii, 704.  
 Leuchs, H., E. Hellriegel, and H. Heering, i, 883.  
 Levaditi, C. See R. Sazerac.  
 Levene, P. A., and G. M. Meyer [with I. Weber], i, 845.  
 Levene, P. A., and H. S. Simms, i, 842.  
 Levin, E. See F. M. Rowe.  
 Lévy, (Mlle) J., i, 860, 861.  
 Liebreich, E., ii, 678.  
 Lingen, J. S. van der, ii, 681.  
 Liverseege, J. F., ii, 714.  
 Long, C. N. H. See M. Copisarow.  
 Lottermoser, A., and R. Lehmann, ii, 688.  
 Lowe, P. See J. C. McLennan.  
 McCall, A. G., and J. R. Haag, i, 911.  
 McClelland, E. W. See S. Smiles.  
 Macgregor, A. M. See A. Hutchinson.  
 Mach, F., and P. Lederle, ii, 718.  
 Machleidt, R. See W. A. Roth.  
 McLennan, J. C., ii, 665, 667.  
 McLennan, J. C., and P. Lowe, ii, 666.  
 McLennan, J. C., and W. W. Shaver, ii, 668.  
 MacTaggart, A., i, 913.  
 Mailhe, A., i, 841.  
 Mannich, C., and S. Kroll, i, 884.  
 Manning, A. B., TRANS., 2079.  
 Margosches, B. M., and R. Baru, ii, 716.  
 Marrack, M. T. See T. S. Moore.  
 Martinet, J., and A. Haehl, i, 854.  
 Matsuno, K. See W. E. Garner.  
 Matulka, N. See F. Henrich.  
 Mauguin, C., ii, 681.  
 Max, F. See H. Biltz.  
 Mayer, M., and H. Zeiss, i, 908.  
 Melander, K. H. A., i, 849.  
 Metcalfe, E. P., and B. Venkateschar, ii, 669.  
 Meyer, G. M. See P. A. Levene.  
 Meyer, K. H. [with H. Hopff and W. Felix], i, 855.  
 Meyer, K. H., and H. Hopff, i, 851.  
 Meyer, K. H., and H. Tochtermann, i, 893.  
 Michaelis, L., and C. Timóñez-Díaz, ii, 682.  
 Milde, E. See F. Arndt.

- Miller, C. W., and J. E. Sweet, ii, 720.  
 Miller, E. J., and C. S. Robinson, ii, 718.  
 Miller, H. G., i, 911.  
 Mills, W. H., and C. R. Nodder, TRANS., 2094.  
 Moerk, F. X., ii, 705.  
 Moir, J., ii, 670.  
 Molander, G., i, 886.  
 Moncada, C. See G. Bargellini.  
 Moore, T. S., M. T. Marrack, and A. K. Proud, i, 865.  
 Morgan, G. T., and T. Glover, i, 854.  
 Morgan, G. T., and W. J. Hickinbottom, i, 868.  
 Morgan, G. T., and D. C. Vining, i, 870.  
 Morse, W., i, 906.  
 Munz, E., i, 909.  
 Mullaly, J. M. See D. L. Hamnick.  
 Murakami, T. See K. Honda.  
 Murayama, Y., i, 875, 876.  
 Murschhauser, H., ii, 715.  
 Myers, C. N., i, 843.  
 NAGAI, S., i, 857.  
 Nakazono, T., ii, 714.  
 Neher, P. See K. Elbs.  
 Neuburger, M. C., ii, 676.  
 Nicolardot, P., and C. Colliguiet, i, 876.  
 Noack, K., i, 910.  
 Nodder, C. R. See W. H. Mills.  
 Nolte, O., i, 914.  
 Oda, K., i, 841.  
 Oddo, G., ii, 691.  
 Oelbermann, G. See E. Knoevenagel.  
 Oldham, J. W. H. See J. C. Irvine.  
 Oliveri-Mandala, E., i, 900; ii, 694.  
 Onohara, K., i, 904.  
 Oppermann, G. See F. Henrich.  
 Ossart, (Mlle) E. See A. Berthelot.  
 Ouwehand, (Mlle) P. See J. Böeseken.  
 PAGET, H. See T. A. Henry.  
 Paolini, V., i, 902.  
 Parker, F. W., i, 911.  
 Partington, J. R., ii, 690.  
 Pascal, P., ii, 692.  
 Passerini, M., i, 895.  
 Pauli, W. See M. Adolf.  
 Péneau, H. See E. Tassilly.  
 Penfold, A. R., i, 859.  
 Perkin, W. H., jun., and S. G. P. Plant, i, 886.  
 Perkin, W. H., jun. See also R. G. Fargher.  
 Perman, E. P. See J. Bonnell.  
 Perren, E. A. See C. K. Ingold.  
 Plant, S. G. P. See W. H. Perkin jun.  
 Ponder, E., i, 905.  
 Pont de Nemours & Co., E. I. du, i, 854.  
 Porter, M. W., i, 886.  
 Powell, A. R. See W. R. Schoeller.  
 Powell, W. J. See C. K. Ingold.  
 Proud, A. K. See T. S. Moore.  
 Pyman, F. L. See R. L. Grant.  
 QUARTAROLI, A., ii, 681.  
 RAMART, (Mme) P. See A. Haller.  
 Rankine, A. O., ii, 690.  
 Rankine, A. O., and C. J. Smith, ii, 694, 696.  
 Raveau, C., ii, 682.  
 Ray, J. N., TRANS., 1959.  
 Raynaud, A., ii, 713.  
 Read, J., and A. C. P. Andrews, i, 861.  
 Reilly, J., i, 846.  
 Rhode, H., i, 909.  
 Rhodes, F. H., and F. E. Haney, i, 857.  
 Rhodes, H. T. F., ii, 681.  
 Rippel, A., i, 912.  
 Rivett, A. C. D., ii, 685.  
 Robertson, J. K., ii, 668.  
 Robinson, C. S. See E. J. Miller.  
 Robl, R. See H. Biltz.  
 Roedel, K. See F. Henrich.  
 Rogers, G. S., ii, 697.  
 Rosa, E. B., E. C. Crittenden, and A. H. Taylor, ii, 704.  
 Rossteutscher, F. See F. Henrich.  
 Roth, A. See W. Borsche.  
 Roth, W. A., R. Macheleidt, and I. Wilms, ii, 709.  
 Rouge, E., i, 911.  
 Roux, E. See E. Tassilly.  
 Rowe, F. M., and E. Levin, TRANS., 2021.  
 Rutherford, (Sir) E., and J. Chawick, ii, 671.  
 Ryschkewitsch, E., ii, 696.  
 SANCHEZ, J. A., ii, 719.  
 Satō, S. See H. Kondō.  
 Sazerac, R., and C. Levaditi, i, 908.  
 Scharnow, B. See J. Eggert.  
 Scheer, K., i, 905.  
 Scheffer, A. See E. Weitz.  
 Schmidt, E., and E. Graumann, i, 912.  
 Schmidt, M. P., and A. Hagerböcker, i, 897.  
 Schneider, W., and F. Kunau, i, 87.  
 Schneider, W., and F. Seebach, i, 859, 877.  
 Schoeller, W. R., and A. R. Powell, TRANS., 1927.

- holl, R. [with H. Hähle], i, 872.  
 hroeter, G., i, 861.  
 humb, W. C. See G. Jones.  
 hwen, G. See W. Steinkopf.  
 ebach, F. See W. Schneider.  
 idel, F. See A. Eckert.  
 rtz, H., ii, 706.  
 annon, E. V., ii, 703.  
 aver, W. W. See J. C. McLennan.  
 eppard, S. E. See F. A. Elliott.  
 imomura, A., and J. B. Cohen,  
 i, 874.  
 uth, W. J. See R. O. Griffith.  
 berrad, O., TRANS., 2029.  
 nms, H. S. See P. A. Levene.  
 mon, K. See H. Lecher.  
 nai, M. See F. Zuckerkandl.  
 ngh, B. K., M. Singh, and J. Lal,  
 TRANS., 1971.  
 ngh, M. See B. K. Singh.  
 öberg, M. See B. Holmberg.  
 nekal, A., ii, 674.  
 niles, S., and E. W. McClelland,  
 i, 880.  
 niles, S., and J. Stewart, i, 861.  
 nith, C. J. See A. O. Rankine.  
 ociety of Chemical Industry in  
 Basle, i, 871.  
 ddy, F., ii, 698.  
 behr, H. A., ii, 714.  
 inkopf, W., and G. Schwen, i, 841.  
 mphenson, R. E., i, 916.  
 ubing, W., ii, 667.  
 wart, J. See S. Smiles.  
 squer, i, 914.  
 dinger, J. See H. Kreis.  
 er, B. C. See Chemische Fabrik  
 Rhenania Akt.-Gcs.  
 hlmann, H. C. See G. Jander.  
 nson, C. O., i, 913.  
 ket, J. E. See C. W. Miller.  
 antoslawski, W., ii, 679.  
 antoslawski, W., and H. i Z.  
 aszkowskie, ii, 680.  
 oke, I. See D. Holde.  
 kegami, S., ii, 698.  
 ailly, E., H. Péneau, and E. Roux,  
 ii, 699.  
 or, A. H. See E. B. Rosa.  
 min, A., ii, 669.  
 oine, E. F., and H. Barthélemy,  
 906.  
 mas, F. See D. F. Twiss.  
 mpson, J. C., ii, 679.  
 Thomson, G. P., ii, 675.  
 thro, W. C., and M. Ehn, i, 908.  
 Timénez-Diaz, C. See L. Michaelis.  
 Tochtermann, H. See K. H. Meyer.  
 Torns, H. See A. Fairbourn.  
 Traube, I., and P. Klein, ii, 683.  
 Travers, ii, 706, 710.  
 Triffitt, P. M. See H. Crompton.  
 Tschernak, G., ii, 703.  
 Twiss, D. F., i, 876.  
 Twiss, D. F., and F. Thomas, i, 876.  
 VECCHIOTTI, L., i, 902.  
 Vegard, L., ii, 674.  
 Venkateschar, B. See E. P. Met-  
 calfe.  
 Vines, H. W. C., i, 905.  
 Vining, D. C. See G. T. Morgan.  
 Vladesco, R. See G. Bertrand.  
 Volk, H. See F. Büdecker.  
 Vorländer, D., i, 867.  
 Vürtheim, A., ii, 710.  
 WALLACE, T., and A. Fleck, ii, 697.  
 Watson, T. L., ii, 701.  
 Weber, I. See P. A. Levene.  
 Weber, S., ii, 699.  
 Wehner, C., i, 845.  
 Weimarn, P. P. von, i, 847.  
 Weiser, H. B., and A. Garrison,  
 ii, 695.  
 Weitz, E., and A. Scheffer, i, 868,  
 869.  
 Wenyon, C. M., i, 908.  
 Wenzel, G. See E. Heuser.  
 Whincop, E. M. See G. M. Bennett.  
 Whitehead, H. R. See P. K. Dutt.  
 Whiteley, J. H. See A. F. Halli-  
 mond.  
 Wieland, H., i, 889.  
 Wilmott, A. J., i, 911.  
 Wilms, I. See W. A. Roth.  
 Wilson, J. A., and E. J. Kern, ii,  
 719.  
 Winsvold, A. See E. Heuser.  
 Winther, C., ii, 670.  
 Wintzell, T. See B. Holmberg.  
 Wood, R. W., ii, 665.  
 Wormall, A. See P. K. Dutt.  
 Wunder, W. See F. Henrich.  
 Wyckoff, R. W. G., ii, 674, 700.  
 ZEISS, H. See M. Mayer.  
 Zuckerkandl, F., and M. Sinai,  
 i, 901.



# ERRATA.

VOL. 119 (TRANS., 1921).

Page	Line	
389	8*	for " <i>cis-Citraconatodiethylenediamine</i> " read " <i>cis-Citraconatodiethylenediaminecobaltic</i> ."
1590	11	for " <i>αγ</i> -dicarboxy- <i>α</i> -methylglutaconate" read " <i>αγ</i> -dicarboxy- <i>α</i> -benzylglutaconate."
1735	14	for " $(C_{11}H_{15}O_6)_2Ca$ " read " $(C_{11}H_9O_7)_2Ca$ ."

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\* From bottom.

Benzene was measured in instruments 2 and 3.

Apparatus.	H. Cm.	a <sup>2</sup> . Sq. mm.	D.	d.	$\gamma$ . Dynes per cm.
2	0.3924	6.708	0.8785	0.0014	28.86
3	0.7294	6.701	„	„	28.83
					Mean 28.85

These results are in excellent agreement with the values found by the workers previously mentioned. For water these values are 72.74 (R. and C.), 72.80 (H. and B.), and for benzene 28.88, 28.79 (R. and C.), 28.88 (H. and B.). This close agreement, however, must be regarded as fortuitous, for it is estimated that the possible errors in the measurements may amount to as much as 0.3 per cent. they are all in the same direction.

### Summary.

- (1) A table of corrections has been constructed which renders possible the use of tubes of any diameter for the measurement of surface tension by the method of capillary rise.
- (2) A simple form of surface tension apparatus has been devised which requires only small amounts of liquid.
- (3) The surface tensions against air at 20.0° of water and benzene have been determined with the following results: Water,  $\gamma = 72.70$ ; benzene,  $\gamma = 28.85$  dynes per cm.

TABLE I.

Values of  $r/b$  for values of  $r/a$  from 0.00 to 2.29.

	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
0.00	1.0000	9999	9998	9997	9995	9992	9988	9983	9979	9974
0.10	0.9968	9960	9952	9944	9935	9925	9915	9904	9893	9881
0.20	0.9869	9856	9842	9827	9812	9796	9780	9763	9746	9728
0.30	0.9710	9691	9672	9652	9631	9610	9589	9567	9545	9522
0.40	0.9498	9474	9449	9424	9398	9372	9346	9320	9293	9265
0.50	0.9236	9208	9179	9150	9120	9090	9060	9030	8999	8968
0.60	0.8936	8905	8873	8840	8807	8774	8741	8708	8674	8640
0.70	0.8606	8571	8536	8501	8466	8430	8394	8358	8322	8286
0.80	0.8249	8212	8175	8138	8101	8064	8026	7988	7950	7913
0.90	0.7875	7837	7798	7759	7721	7683	7644	7606	7568	7529
1.00	0.7490	7451	7412	7373	7334	7295	7255	7216	7177	7137
1.10	0.7098	7059	7020	6980	6941	6901	6862	6823	6783	6744
1.20	0.6704	6665	6625	6586	6547	6508	6469	6431	6393	6354
1.30	0.6315	6276	6237	6198	6160	6122	6083	6045	6006	5968
1.40	0.5929	5890	5851	5812	5774	5736	5697	5659	5621	5583
1.50	0.5545	5508	5471	5435	5398	5362	5326	5289	5252	5216
1.60	0.5179	5142	5106	5070	5034	4998	4963	4927	4892	4857
1.70	0.4822	4787	4753	4719	4686	4652	4618	4584	4549	4514
1.80	0.4480	4446	4413	4380	4347	4315	4283	4250	4217	4184
1.90	0.4152	4120	4089	4058	4027	3996	3965	3934	3903	3873
2.00	0.3843	3813	3783	3753	3723	3693	3663	3633	3603	3574
2.10	0.3546	3517	3489	3461	3432	3403	3375	3348	3321	3294
2.20	0.3267	3240	3213	3186	3160	3134	3108	3082	3056	3030

TABLE II.

Values of  $r/b$  for larger values of  $r/a$ .

	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
2.0	0.384	355	327	301	276	252	229	206	185	166
3.0	149	133	119	107	097	088	081	074	067	061
4.0	056	051	047	043	039	035	031	028	025	022
5.0	020	018	017	015	014	012	010	009	008	007
6.0	006	006	005	004	004	003	003	003	002	002

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LONDON, E.C.4.

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CLXXVI.—*Contributions to the Chemistry of the Terpenes. Part XX. The Action of Hypochlorous Acid on Pinene.*

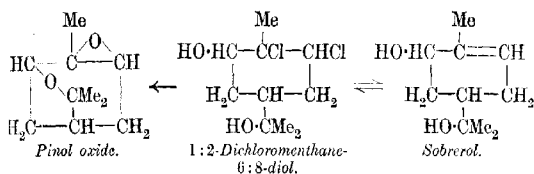
By GEORGE GERALD HENDERSON and JOSEPH KENNETH MARSH

THE action of hypochlorous acid on pinene has been examined by Wagner and his collaborators (Wagner and Slawinski, *Ber.*, 1896, **32**, 2064; Wagner and Ginsberg, *Ber.*, 1896, **29**, 886; Ginsberg *J. Russ. Phys. Chem. Soc.*, 1898, **30**, 686), but by modifying the method of carrying out the reaction we have obtained results which differ in several respects from those already published.

Wagner and Slawinski treated a cooled mixture of *l*-pinene and 10 per cent. aqueous acetic acid with a 2 per cent. aqueous solution of sodium hypochlorite in such proportions that rather more than two molecules of hypochlorous acid were present for each molecule of pinene. After completion of the reaction, the solution was separated from some undissolved oil, mixed with excess of potassium hydroxide, and, after standing for two or three days, saturated with carbon dioxide and extracted with ether. From the ethereal solution the following products were separated: a chlorohydrin,  $C_{10}H_{17}O_2Cl$ , m. p.  $31^\circ$ ; traces of a different chlorohydrin; pinic oxide; sobrerithritol; nopinol glycol; and some unsaturated compounds, not further examined. Our own work has shown that these substances are not the primary products of the reaction, but are formed from these by the action of potassium hydroxide. Moreover, when Wagner and Slawinski modified their procedure by omitting the treatment of the reaction mixture with alkali hydroxide, they obtained from 300 grams of pinene about 140 grams of a viscous oil, from which they separated about 20 grams

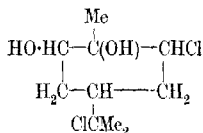
of a crystalline pinene dichlorohydrin, m. p. 136–137°; the oily residue on treatment with dilute potassium hydroxide yielded some of the chlorohydrin of m. p. 131°, and some sobrerithritol.

Treatment of pinene with successive quantities of a very dilute aqueous solution of hypochlorous acid yielded two crude products, one of which was extracted from the aqueous solution, whilst the other was insoluble in water. The soluble product proved to be a mixture of three crystalline dichlorohydrins,  $C_{10}H_{18}O_2Cl_2$ , which melted at 139–140°, 124–126°, and 155° respectively, together with a viscous, oily substance. The reactions of the first of these dichlorohydrins are identical with those of the compound of m. p. 136° prepared by Wagner and Slawinski, who found it to be optically active, to yield pinol oxide on treatment with aqueous potassium hydroxide, and to be converted into sobrerol when treated with zinc dust and alcohol. For these reasons, they concluded that the so-called pinene dichlorohydrin is, in fact, sobrerol dichloride or *cis*-1:2-dichloromenthane-6:8-diol,



We have confirmed this view of the constitution of the pinene dichlorohydrin of m. p. 139° by its direct synthesis from *i*-sobrerol by the addition of chlorine.

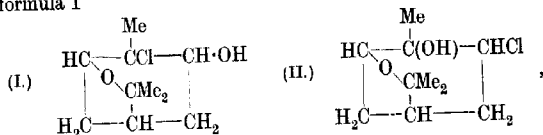
The second pinene dichlorohydrin, which melts at 124–126°, is optically active. Of the four possible structurally different dichlorohydrins, only two can show optical activity. One of these has been proved to be sobrerol dichloride; the other must be the compound under discussion, which therefore must be



2:8-Dichloromenthane-1:6-diol.

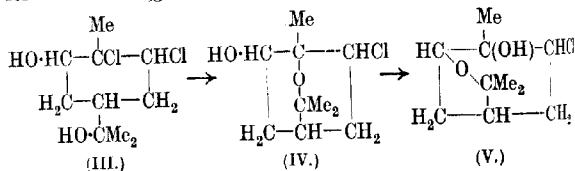
As regards the third dichlorohydrin of m. p. 155°, the quantity isolated was very small, and we have no direct evidence of its constitution. It is optically active, and may perhaps be derived from  $\beta$ -pinene, a little of which may possibly have been present in the specimen of pinene used.

On treatment with two molecular proportions of aqueous potassium hydroxide, the dichlorohydrin of m. p. 139° yields pinol oxide and *i*-pinol glycol 2-chlorohydrin,  $C_{10}H_{17}O_2Cl$ , m. p. 104–105°. The latter compound has been proved (Ginsberg and Wagner, *J. Russ. Phys. Chem. Soc.*, 1898, **30**, 675) to be the racemic form of the optically active chlorohydrin which melts at 131°. It is very stable towards aqueous potassium hydroxide in the cold, but on heating it is converted, with some resinification, into pinol oxide. On treatment with zinc dust and alcohol it yields pinol, by loss of a chlorine atom and a hydroxyl group. It cannot have the formula I



for this represents the structure of the isomeric pinol glycol 1-chlorohydrin, m. p. 52–54°, which was prepared by the action of hypochlorous acid on pinol and proved to contain a secondary alcohol group (Ginsberg, *J. Russ. Phys. Chem. Soc.*, 1898, **30**, 681). Hence it must be pinol glycol 2-chlorohydrin (II).

An isomeric chlorohydrin, quite different in properties from the above, is produced when the dichlorohydrin of m. p. 139° is agitated with very dilute aqueous potassium hydroxide in the proportion of 1 mol. of KOH to 1 mol. of  $C_{10}H_{17}O_2Cl_2$ . This substance is a crystalline solid which melts at 70–71°; the chlorine content agrees with the formula  $C_{10}H_{17}O_2Cl$ . Its constitution could not be directly elucidated owing to the ease with which it is transformed into the stable *i*-pinol glycol chlorohydrin of m. p. 104° by the action even of water, but in all probability it is an isomeric chlorohydrin. Indeed the conversion of pinene dichlorohydrin, m. p. 139° (III), into pinol glycol 2-chlorohydrin (V) cannot take place in a simple manner, and is more easily understood if it be assumed that the first step is the formation of this intermediate compound for which we suggest the following formula (IV).



The fact that this intermediate compound, unlike pinol glycol 2-chlorohydrin, is capable of forming a nitrobenzoate, yields support

on this view. The same formula has been suggested by Ginsberg (*loc. cit.*) for a chlorohydrin which he obtained by the action of potassium hydroxide on the syrupy product of the treatment of pinene with hypochlorous acid, but the available data are not sufficient to decide whether or not the two substances are the same.

Part of the viscous residue from which the crystalline dichlorohydrins had been separated was distilled under diminished pressure, but much decomposition took place, and no satisfactory result was obtained. Another portion, on treatment with 10 per cent. aqueous potassium hydroxide, yielded crystals of pinol glycol, m. p. 124°, which was undoubtedly formed from pinol oxide, the primary product of the action of alkali hydroxide on some dichlorohydrin still present in the residue, when the alkaline solution was acidified.

Fractional distillation under diminished pressure of the oily product which was not dissolved by water yielded some unchanged pinene and some tricyclene dichloride,  $C_{10}H_{16}Cl_2$ , the presence of which among the substances formed by the action of hypochlorous acid on pinene had already been observed by Ginsberg and Wagner (*loc. cit.*).

It is evident from the results quoted that the action of hypochlorous acid, even when in very dilute solution, is similar to that of many other reagents to the extent that it effects disruption of the very unstable dimethylcyclobutane ring in pinene. Hence the products of the reaction are in reality derivatives of menthane and not of pinene.

#### EXPERIMENTAL.

##### *Preparation of Pinene Dichlorohydrins, $C_{10}H_{18}O_2Cl_2$ .*

The pinene used in our experiments was prepared from American turpentine by steam distillation and subsequent fractionation. It boiled at 156–157° and was slightly dextrorotatory. A dilute solution of hypochlorous acid, prepared by Taylor's method (T., 12, 101, 444), was shaken with a quantity of pinene in a large bottle. Absorption of the acid took place rapidly, and when complete the mixture was left until the oily layer had separated. In order to obtain good yields of the dichlorohydrins their aqueous solutions should not be kept for any long time. The aqueous layer was syphoned off and saturated with sodium chloride, with the result that part of the product separated in solid form. This was collected and the filtrate thoroughly extracted with ether. The unattacked pinene was repeatedly agitated with fresh quantities

of hypochlorous acid until practically no more of the acid was taken up. As the process went on, the oily layer became by degrees denser and more viscous, developing a tendency to form emulsions, and in order to prevent this a little light petroleum was added. When the treatment with hypochlorous acid was stopped, the greater part of the original pinene had passed into solution in the water, but there remained a quantity of an oily insoluble product, which was collected and examined separately.

The mixed ethereal solutions of the soluble products were dried over anhydrous sodium sulphate, and on removal of the ether by distillation a syrupy liquid was left, from which a crystalline deposit separated on standing. The crystals were freed from the oily matter as far as possible with the aid of the filter-pump. Further deposition of crystals from the filtrate took place, and this continued for a considerable time, although separation of the crystals from the viscous oil became increasingly difficult. Finally most of the original syrupy substance was obtained in a crystalline form. The collected crops of crystals were washed with a little ether and repeatedly recrystallised from that solvent, with the result that we finally obtained a less soluble dichlorohydrin which melted at  $139^{\circ}$ , and a more soluble, of m. p.  $124-126^{\circ}$ .

*Sobrerol dichloride* (1:2-dichloromenthane-6:8-diol) crystallises from ether in small prisms. It melts at  $139-140^{\circ}$ , and can be distilled under diminished pressure with only slight decomposition. It is sparingly soluble in cold ether, almost insoluble in light petroleum, and very readily soluble in alcohol. In water, it dissolves rather sparingly in the cold, more easily on heating, but undergoes decomposition to some extent. It is readily attacked by cold dilute solutions of alkali hydroxides, losing a chlorine and a hydrogen atom and yielding in the first instance the chlorohydrin of m. p.  $104^{\circ}$  (Found: Cl = 29.49.  $C_{10}H_{18}O_2Cl_2$  requires Cl = 29.46 per cent.).

The *nitrobenzoate*, prepared as usual in pyridine solution, is very sparingly soluble in alcohol, but is easily purified by crystallisation from a mixture of acetone and water, from which it separates as a colourless, crystalline powder which melts at  $175^{\circ}$ .

In order to confirm Wagner's view of the constitution of the dichlorohydrin, a solution of chlorine in dry chloroform was added gradually to a similar solution of sobrerol, and the solvent removed by evaporation in a vacuum desiccator. A viscous liquid remained from which crystals separated on standing. The crystals were washed with a little ether, and after recrystallisation from that solvent were found to melt at  $138^{\circ}$ ; a mixture of these with the dichlorohydrin of m. p.  $139^{\circ}$  had the same melting point.

ence it is evident that this dichlorohydrin is really *sobrerol* chloride.

The *dichlorohydrin* of m. p. 124–126°, which apparently is 8-dichloromenthane-1 : 6-diol, was separated from the isomeride so mentioned by taking advantage of its greater solubility in ether. It crystallises in colourless, silky needles, of which the solubility in water, alcohol, and light petroleum is much the same as that of *sobrerol* dichloride. Like the latter, it reacts readily with dilute aqueous alkali hydroxides, but it yields directly the optically active pinol glycol 2-chlorohydrin of m. p. 131°, with a trace of pinol oxide. The formation of an intermediate compound, which happens with *sobrerol* dichloride, was not observed under any conditions. This dichlorohydrin is levorotatory; one specimen gave  $[\alpha]_{D}^{20} = -28.2^\circ$ .

A number of different fractions of crude pinene dichlorohydrin which had been prepared before the war were mixed and dissolved in hot benzene. On cooling the solution, a mass of fine, silky needles, consisting mainly of the dichlorohydrin of m. p. 124–126°, separated, together with some large, well-defined crystals. When the solution was warmed, the needles dissolved, but the bulk of the larger crystals remained behind, and was easily separated by decanting the liquid. After several recrystallisations from hot benzene, in which it is sparingly soluble, this *dichlorohydrin* was obtained in lustrous, colourless prisms melting at 155°. It is optically active,  $[\alpha]_{D}^{20} = -59.5^\circ$ . Like the other dichlorohydrins, it reacts with dilute aqueous alkali hydroxides, but yields a product different from either of those obtained from the former. As it appeared possible that this substance might have been formed from the dichlorohydrin of m. p. 124° by heating in benzene, this was put to the test of experiment, but even after prolonged heating the result was negative. Curiously enough, no trace of this compound could be detected in the specimens of dichlorohydrins recently prepared, although the same oil of turpentine was in each case used as the source of the pinene, and the methods of treatment were the same.

#### *Preparation of the Chlorohydrins, C<sub>10</sub>H<sub>17</sub>O<sub>2</sub>Cl.*

12.2 Grams (1 mol.) of *sobrerol* dichloride were added to a 1 per cent. aqueous solution of 5.7 grams (2 mols.) of potassium hydroxide and left for four days with occasional shaking. On the third day, crystals of pinol glycol chlorohydrin separated, and on the fourth day almost all the dichlorohydrin had passed into the solution, which was now neutral. The solution was saturated with sodium



chloride and extracted with ether. From the ethereal extract, 4.3 grams of a crystalline solid were obtained together with a quantity of a liquid with a strong, characteristic odour, which distilled at 78–80°/16 mm. When shaken with 2 per cent. aqueous sulphuric acid, the liquid passed into solution, and from the solution a quantity of crystals of pinol glycol, m. p. 124°, was extracted by means of ether. The liquid was thus proved to be pinol oxide. The solid product, the racemic form of pinol glycol 2-chlorohydrin, was purified by crystallisation from light petroleum, from which it separated in stout, colourless prisms, m. p. 104–105°. It is readily soluble in ether, alcohol, or acetone, from the last of which it crystallises very well, and fairly so in water, and in hot light petroleum.

When sobrerol dichloride is treated with only one proportion of potassium hydroxide, the reaction takes a different course. 16.2 Grams (1 mol.) of the dichloride, reduced to very fine powder, were added to a 0.5 per cent. aqueous solution of 3.7 grams (1 mol.) of potassium hydroxide, and the mixture was stirred continuously. In about three hours the solution had become neutral, and all but a little of the dichloride was dissolved. The solution was filtered, the filtrate saturated with sodium chloride and extracted with ether, and the ethereal extract washed with water, dried over anhydrous sodium sulphate, and distilled. There remained an oily substance which solidified after thorough drying in a vacuum desiccator, but in this case no pinol oxide was produced. The solid, which weighed 13.5 grams, was broken up, washed once or twice with a little light petroleum, and recrystallised from that solvent. When pure, this new *chlorohydrin* crystallises in radiating tufts of fine needles, which melt at 70°. It is only sparingly soluble in light petroleum, even in the heat, but dissolves very easily in other organic solvents and to some extent in water (Found: C = 58.7; H = 8.5; Cl = 17.5.  $C_{10}H_{17}O_2Cl$  requires C = 58.7; H = 8.3; Cl = 17.3 per cent.).

Unlike pinol glycol chlorohydrin, this compound reacts with *p*-nitrobenzoyl chloride in pyridine solution, yielding a crystalline *p*-nitrobenzoate, which separates from alcohol in small, colourless crystals, m. p. 125°. It is very easily soluble in acetone, and sparingly soluble in alcohol.

This chlorohydrin is very easily transformed into *i*-pinol glycol chlorohydrin, m. p. 104°. The change is quickly effected if the chlorohydrin is left in contact with dilute solutions of alkali hydroxides, a little pinol oxide being also produced in this case, or if it is mixed with very dilute sulphuric acid. If an aqueous solution of the compound is left to evaporate at the ordinary temperature,

crystals of *i*-pinol glycol chlorohydrin separate. It may be dissolved in glacial acetic acid without undergoing this transformation, but when an attempt was made to oxidise it with chromic anhydride in acetic acid solution, pinol glycol chlorohydrin was again produced.

The pinene dichlorohydrin of m. p.  $124^{\circ}$  was treated with one molecular proportion of potassium hydroxide in exactly the same way as *sobrerol* dichloride, but in no case was the chlorohydrin of m. p.  $70^{\circ}$  or any analogous intermediate compound obtained. The product consisted of the optically active pinol glycol 2-chlorohydrin, crystallising in lustrous needles of m. p.  $131^{\circ}$ , together with some of the inactive form, m. p.  $104^{\circ}$ . A trace of pinol oxide could also be detected and slight resinification occurred. This dichlorohydrin was also treated with moist silver oxide and with silver acetate in alcoholic solutions; in each case pinol oxide was produced along with a considerable amount of resinous matter. Oxidation with chromic acid mixture and with chromic anhydride in acetic acid gave no definite results, and attempts to prepare a *p*-nitrobenzoate were unsuccessful.

#### *The Product insoluble in Water.*

The oily product of the action of hypochlorous acid on pinene which remained undissolved by water was heated to remove light petroleum and then distilled at 14 mm. pressure. Fractions boiling at  $80$ – $90^{\circ}$ ,  $125$ – $130^{\circ}$ , and  $130$ – $145^{\circ}$  were collected. When the temperature reached  $105^{\circ}$ , decomposition began, with evolution of hydrogen chloride, and a large residue of pitchy material was left in the flask. The liquid fraction of b. p.  $80$ – $90^{\circ}$  was redistilled under atmospheric pressure, but much decomposition ensued and no definite product, except some unchanged pinene, was isolated. The fractions of higher boiling point, principally that distilling between  $125^{\circ}$  and  $130^{\circ}$ , deposited a crystalline solid on standing, and additional quantities of this were obtained by refractionation of the liquid portions. The solid was washed with light petroleum and recrystallised. From ether, in which it is readily soluble, it separates in large, colourless plates which melt at  $176^{\circ}$ ; from methyl alcohol it crystallises in leaflets, m. p.  $169$ – $172^{\circ}$ ; in cold water it is almost insoluble (Found: Cl = 34.2.  $C_{10}H_{16}Cl_2$  requires Cl = 34.2 per cent.). The compound was thus identified as tricyclene dichloride, although the melting point of our specimen was higher than that ( $165$ – $168^{\circ}$ ) quoted by Ginsberg and Wagner. Additional proof was provided by its conversion into camphane (Semmler, *Ber.*, 1900, **33**, 774, 3420). Tricyclene dichloride in

alcoholic solution is not readily attacked by sodium, but on prolonged treatment it yielded a crystalline solid which melted at 154–155°, boiled at 160–162°, sublimed very easily in small, lustrous plates, and behaved as a saturated compound towards bromine and towards potassium permanganate; the solid, in short, was camphane.

We take this opportunity of expressing our thanks to the Department of Scientific and Industrial Research and also to the Research Fund Committee of the Carnegie Trust for grants which have defrayed the expense of this work. We wish also to acknowledge the help of Mr. J. W. Tait in some of the earlier experimental work.

UNIVERSITY OF GLASGOW.

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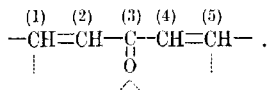
# CLXXVII.—*The Reactivity of Doubly-conjugated Unsaturated Ketones. Part I. 4'-Dimethylamino-2-hydroxydistyryl Ketone.*

By ISIDOR MORRIS HEILBRON and JOHANNES SYBRANDT BUCK.

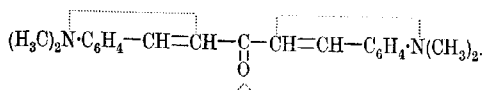
As the result of an investigation of the action of compounds possessing a reactive methylene group on ketones containing the system  $\cdot\text{C}:\text{C}-\text{C}:\text{C}\cdot$ , such as distyryl ketone, *pp'*-tetramethyldiamino-

$\overset{\text{O}}{\parallel}$   
distyryl ketone, etc., Borsche (*Annalen*, 1910, **375**, 145), basing his views on the Thiele conception of residual affinity, drew conclusions which more fully account for the varied degree of activity of these substances. Whereas distyryl ketone readily reacts with ethyl acetoacetate or acetylacetone in presence of piperidine, *pp'*-tetramethyldiaminodistyryl ketone is quite unreactive under similar conditions, whilst *p*-dimethylaminodistyryl ketone only reacts with difficulty.

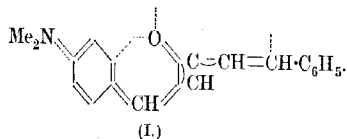
According to Borsche, the reactivity of distyryl ketone is due to the large amount of free residual affinity on both the carbonyl oxygen atom and the two external carbon atoms of the conjugated system:



The inactivity of the *pp'*-tetramethyldiamino-derivative is accounted for by assuming neutralisation of the free affinities of the end carbon atoms with the unsaturated nitrogen atoms of the dimethylamino-groups.



As this, however, does not in itself explain the diminished reactivity of *p*-dimethylaminodistyryl ketone, the further assumption is made that the disturbing influence of the dimethylaminophenyl residue also affects the unsaturation of the oxygen atom in such a way that a neutralisation resulting in complex ring formation takes place:



Although these postulates clearly demonstrate the mutual influence of groups or atoms upon each other, the explanation is not, however, complete. This may readily be demonstrated by a consideration of the above formula, where it follows that substitution in the phenyl group would not be expected to influence the activity of the molecule to any great extent, other than in the para-position, where it would tend, through neutralisation of free affinity, to cause decreased reactivity, as exhibited by *pp'*-tetramethyldiaminodistyryl ketone.

The present authors have now prepared 4'-dimethylamino-2-hydroxydistyryl ketone, and find that it actually exhibits a quite extraordinarily enhanced reactivity, being almost comparable to triphenylmethyl in the ease with which it forms additive products. Before entering into a discussion of the views which we suggest in order to account for this, the preparation and properties of the substance will first be briefly discussed. By the condensation of 2-hydroxystyryl methyl ketone with *p*-dimethylaminobenzaldehyde in alcoholic solution in presence of 10 per cent. sodium hydroxide, a deep blood-red solution is formed, which, on standing, often deposits a small quantity of an orange-red, crystalline substance melting at 194°, which is identical with *pp'*-tetramethyldiaminodistyryl ketone (Sachs and Lewin, *Ber.*, 1902, **35**, 3576).

By largely diluting the mother-liquors with water, there gradually separates out a precipitate which crystallises from alcohol in brick-

red prisms melting at 143°. After removal of this substance, further dilution yields a small quantity of orange crystals, which form round the sides of the containing vessel and melt at 200°. The yield of these substances varies enormously, the reaction being extremely sensitive to very minute alterations of the conditions, such as slight variation of the room temperature or small differences of alkali concentration. In a normal reaction, the compound of m. p. 143° forms practically the total yield, but sometimes, on the other hand, none of this substance can be isolated, only a heavy tar being precipitated on dilution of the reaction mixture. In other preparations, considerable quantities of *pp'*-tetramethyldiaminodistyryl ketone resulted, even when precautions were taken to maintain the conditions as regards concentration as constant as possible. It was anticipated that the compound melting at 143° would be 4'-dimethylamino-2-hydroxydistyryl ketone, but analysis proved it to be, not the free ketone, but an additive product containing one molecule of *p*-dimethylaminobenzaldehyde. Condensation experiments were accordingly carried out, using increased quantities of *o*-hydroxystyryl methyl ketone in the hope of obtaining the free ketone, but the only effect of this was to decrease the amount of the *p*-dimethylaminobenzaldehyde additive product. Experience has shown that the highest yield of this compound is got by using 1 mol. of the ketone to 1.5 mols. of the aldehyde, when a yield equal to the weight of the *p*-dimethylaminobenzaldehyde used can be obtained.

On heating this additive compound with benzene, the brick-red crystals rapidly undergo change, without complete solution taking place, being converted into glistening, puce-coloured crystals melting at 154°. This substance is an additive product of the hydroxy-ketone with 0.5 mol. of benzene, from which it cannot be freed even on long heating at 100°. Repeated crystallisation of this benzene additive product from boiling absolute alcohol ultimately results in the replacement of the 0.5 mol. of benzene by 1 mol. of alcohol. Most other solvents appear to act similarly, an exception being ethyl acetoacetate, from which the solvent-free ketone is obtained.

The table on page 1503 gives a list of typical additive products and it will be observed that the colour of these varies from yellow to blue, green, and almost black. In certain cases, the most noticeable being in the chloroform additive product, chromotropic varieties have been isolated.

The free ketone, which is most readily obtained by heating the alcohol additive product at 100°, forms, under these conditions, a dull crimson, crystalline powder. Other coloured varieties have

also been isolated by methods described in the experimental part, but the differences in colour are not especially strongly marked, and all produce a red streak. That, however, the forms are not altogether identical is shown by the fact that, whilst the brilliant scarlet variety obtained from ethyl acetoacetate readily combines in alcoholic solution with *p*-dimethylaminobenzaldehyde, the reddish-black modification obtained from ethyl acetate-heptane is unreactive. It must therefore be concluded that the free ketone can exist in different phases, and that these retain their special configuration, at least temporarily, even in solution. It consequently follows that the addenda must differ to some extent in the manner in which they are united to the ketone, and this, we consider, determines the colour of the "solvate."

Addendum.	Composition.	Colour.
Ethyl alcohol	$C_{15}H_{15}O_2N, C_7H_5O$	purplish-black
Ethyl acetate	$\frac{1}{2}C_6H_5O_2$	bluish-black
Benzene	$\left\{ \begin{array}{l} \text{,, } C_6H_6 \\ \text{,, } \frac{1}{2}C_6H_4 \end{array} \right.$	$\left\{ \begin{array}{l} \text{almost black} \\ \text{pnceo} \end{array} \right.$
Chloroform	$\text{,, } CHCl_3$	$\left\{ \begin{array}{l} \text{bright red} \\ \text{indigo-blue} \end{array} \right.$
<i>m</i> -Dinitrobenzene	$\text{,, } C_6H_4(NO_2)_2$	reddish-violet
2 : 4 : 6-Trinitrotoluene	$\text{,, } 2C_7H_5(NO_2)_3$	reddish-brown
<i>p</i> -Benzoquinone	$\text{,, } C_6H_4O_2$	greenish-black
Benzene and acetic acid	$2C_{15}H_{15}O_2N, \frac{1}{2}C_6H_5, \frac{1}{2}C_2H_4O$	indigo-blue
Phenol	$C_{15}H_{15}O_2N, C_6H_5 \cdot OH$	bluish-black
Phenanthrene	$\text{,, } \frac{1}{2}C_{15}H_{10}$	emerald green
Fluorene	$\text{,, } \frac{1}{2}C_{15}H_{10}$	bright green
Fluorene and methyl alcohol	$\text{,, } \frac{1}{2}C_{15}H_{10}, CH_3 \cdot OH$	dark red
Carbazole	$\text{,, } C_{12}H_9N$	crimson
<i>p</i> -Dimethylaminobenzaldehyde	$\text{,, } C_9H_{11}ON$	$\left\{ \begin{array}{l} \text{brick-red} \\ \text{light yellow} \end{array} \right.$

*pp'*-Tetramethyldiaminodistyryl Ketone.—The presence of this substance in the condensation reaction mixture can only be accounted for by assuming a complete scission of part of the *o*-hydroxystyryl methyl ketone. In support of this, Decker and Felsner (*Ber.*, 1908, **41**, 2997) have shown that both 2 : 2'-dihydroxydistyryl ketone and *o*-hydroxystyryl methyl ketone, when treated with alkali in the heat, are readily hydrolysed to salicylaldehyde and acetone. We have confirmed this, and find, further, that *o*-hydroxystyryl methyl ketone is broken up even by cold alkali of moderate concentration, the constituents then largely recombining to give 2 : 2'-dihydroxydistyryl ketone, which crystallises out in the form of its sparingly soluble sodium salt. We have further ascertained that, under similar conditions, *p*-dimethylaminostyryl methyl ketone gives the corresponding symmetrical *pp'*-tetramethyldiaminodistyryl ketone. A somewhat different type of reaction is to be recorded in the formation of *pp'*-dimethoxydistyryl ketone by the interaction of *o*-hydroxystyryl methyl ketone with

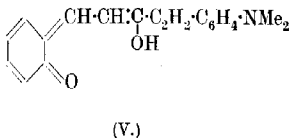
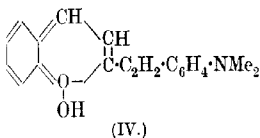
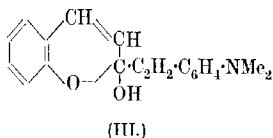
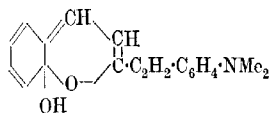
anisaldehyde in the presence of alkali. Finally, a saturated alcoholic solution of the *p*-dimethylaminobenzaldehyde additive compound, when left to stand in the presence of alkali, readily yields both *pp'*-tetramethyldiaminodistyryl ketone and the substance melting at 200°. These reactions seemingly follow the ordinary laws of mass action, the tendency in all cases being towards the formation of the corresponding symmetrical and usually less soluble derivative or its salt.

*Compound Melting at 200°*.—As this compound can readily be broken down by means of dilute aqueous alcohol in the heat into the hydroxy-ketone (m. p. 154°) and salicylaldehyde, experiments were accordingly undertaken to synthesise it directly from its constituents. By crystallising the free hydroxy-ketone from salicylaldehyde, deep red prisms, melting unsharply at 135°, are formed, which contain one-half molecule of salicylaldehyde. On the other hand, from an alcoholic solution of molecular proportions of the constituents, in presence of aqueous alkali, the compound melting at 200° separates out. This substance invariably contains sodium, but despite innumerable experiments having been carried out, no absolutely definite stoichiometric relationship between the sodium and the other constituents has been established. Specimens of the product repeatedly recrystallised from absolute alcohol give analytical results which point to a compound containing one atom of sodium combined with one molecule of the hydroxy-ketone and one-half molecule of salicylaldehyde. That the production of this compound is not due to simple salt formation with the hydroxyl group of the salicylaldehyde is readily proved by the formation of completely analogous compounds from benzophenone. In absence of alkali, an additive product, melting between 137° and 143°, containing one-half molecule of benzophenone, is produced, whereas if sodium hydroxide is present a product which melts at 197° and contains approximately one atom of sodium in addition to the benzophenone is obtained. We are of the opinion that in these two compounds the sodium atom forms part of the inner complex (Formula VI), and that by its presence the salicylaldehyde or benzophenone addendum becomes more firmly attached. It is interesting to note that no sodium salt of the hydroxy-ketone itself has been isolated.

*4'-Dimethylamino-2-methoxydistyryl Ketone*.—In order to determine whether the outstanding properties of the hydroxy-ketone were due solely to substitution in the ortho-position or also to the specific properties of the hydroxyl group, the corresponding methyl ether was prepared. This substance, which can be obtained both in red and yellow forms melting at 95°, differs essentially in properties

rom the hydroxy-ketone, no longer possessing the power of forming additive products with solvents, aldehydes, *p*-benzoquinone, etc. On the other hand, it is still capable of combining with substances containing strongly negative groups, such as the polynitro-compounds.

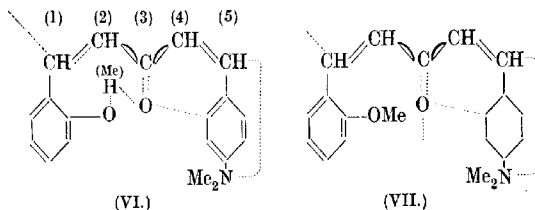
It is thus evident that the primary cause of the enhanced activity exhibited by the hydroxy-ketone is directly due to the presence of the hydroxyl group. In attempting to arrive at an explanation concerning this, the possibility of attributing different structures to the free ketone and the methyl ether was considered, for it is obviously easy to imagine a rearrangement of the ortho-substituted hydroxy-compound either into benzopyrylium bases or into an open-chain ortho-quinonoid derivative, as indicated by the following formulae :



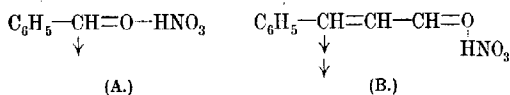
Of these, II, III, and IV can be immediately rejected as not harmonising with the experimental results recorded in our second communication, where it is shown that the ketone forms both a hydroxylamino-derivative and a hydroxylamino-oxime (this vol., p. 1515). Similarly, V would be expected to yield only the normal oxime, but even if such a formula did actually represent the structure of the hydroxy-ketone, the difficulty would still remain, for a spectrographic examination of the two substances in alcoholic solution has shown that, in solution, at any rate, they possess identical structure, both having very similar absorption spectra with two well-defined bands at  $1/\lambda = 2300$  and  $3546\mu\mu$ . An explanation must therefore be sought in other directions, and this we suggest may be found by taking into account, not alone the neutralisation processes advanced by Borsche (*loc. cit.*), but also the effect of such on the central carbonyl group of the crossed conjugated system. According to Pfeiffer's theory of halochromy (*Annalen*, 1910, **376**, 285; 1911, **383**, 92), the more the residual affinity of the carbonyl oxygen atom is neutralised, the more pronounced becomes the unsaturation



on the carbon atom of this group. Hence, if for any reason, in *p*-dimethylaminodistyryl ketone (I), that portion of the residual affinity on the carbonyl oxygen atom not used up in the first complex ring formation were to become neutralised, more free affinity would appear on C(3). This process, we suggest, takes place in 4'-dimethylamino-2-hydroxydistyryl ketone through the formation of a second ring system involving the hydroxyl group and carbonyl oxygen atom (VI),



as a result of which the conjugated linking between C(3) and C(2) becomes intensified\* at the expense of the ethenoid linking between C(2) and C(1). The final effect of this is to enhance to a very high degree the free affinity on the external atom, C(1), of the conjugated system and it is at this unsaturated centre that we consider addenda become attached in the first place. A similar conclusion has been drawn by Reddelien (*J. pr. Chem.*, 1915, [ii], **91**, 213) from his study of the additive products of nitric acid and various aldehydes and ketones. Thus, whilst benzaldehyde nitrate (A) is very unstable, the nitrate of cinnamaldehyde (B) is comparatively stable on account of the intensified partial valency.



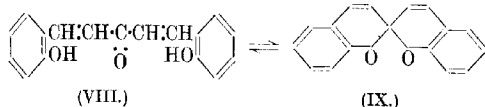
It has frequently been observed that where inner complex formation is possible the effect only becomes fully operative on the replacement of hydroxyl hydrogen by a metallic atom such as sodium. The action of alkali on *p*-dimethylamino-2-hydroxydistyryl ketone may also be interpreted as an intensification of the co-ordinated system, whereby a still higher degree of unsaturation is attained, with consequent greater stability of the partial valency additive products.

As regards the formation of a heterocyclic ring containing eight atoms, which assumption is a necessary deduction from our postulates, Werner (*Ber.*, 1908, **41**, 1062), in the development of

\* The effect does not act between C(3) and C(4), as this whole system is in a state of equilibrium,

his theory of mordant colours, suggests that the inability of phenyl *o*-hydroxystyryl ketone to form lakes with metallic bases is due to the difficulty of obtaining complex ring formation in systems in which more than six atoms are involved. It seems to us, however, that in a system where actually only five carbon atoms are involved this difficulty is more apparent than real, for it is quite conceivable

that the grouping  $\begin{smallmatrix} \text{H} \\ | \\ -\text{O}-\text{O}- \end{smallmatrix}$  approximates spatially to but one carbon atom. The ready transformation of 2:2'-dihydroxydistyryl ketone (VIII), on warming, into dibenzospiropyran (IX) (Decker and Felser, *loc. cit.*) would seem to support this view of close grouping.

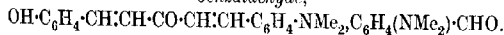


In the case of the methyl ether (VII) the valence distribution is substantially altered, the methoxy-group having no effect on the carbonyl oxygen atom, which consequently still retains a certain degree of free residual affinity, enabling the normal reactions of that group to become operative. In the same way, that the external carbon atom, C(1), although not possessing sufficiently enhanced free affinity to form subsidiary valence products with all addenda, is nevertheless capable of reacting in favourable circumstances, is evident from the formation of the additive compounds with dinitro- and trinitro-benzene. It is reasonable to assume that in solution 4'-dimethylamino-2-methoxydistyryl ketone is actually present as a solvate additive product.

This investigation is being extended in other directions, such as the examination both of the pyranol salts and the metallic complexes. At the same time, work is being continued with other ketones and aldehydes with the view of obtaining evidence of the effect of different substituents in the benzene nuclei.

#### EXPERIMENTAL.

##### 4'-Dimethylamino-2-hydroxydistyryl Ketone + *p*-Dimethylamino-benzaldehyde,



An alcoholic solution containing 16 grams (1 mol.) of *o*-hydroxystyryl methyl ketone and 22 grams (1.5 mols.) of *p*-dimethylamino-benzaldehyde was treated with 80 c.c. of 10 per cent. sodium hydroxide (2 mols. of NaOH). The solution, which immediately

acquired a blood-red colour, was kept at room temperature for two to three days and then diluted to 4000 c.c. with water. The brick-red, flocculent precipitate which gradually separated was filtered off and purified by crystallisation from absolute alcohol. The substance was obtained in thick, brick-red prisms, melting with vigorous decomposition at  $143^{\circ}$ . It is moderately soluble in methyl or ethyl alcohol or ethyl acetate, but is decomposed by benzene, chloroform, or ether. The yield obtained by the above method equals the weight of the dimethylaminobenzaldehyde taken, and is higher than that obtained when any other proportions of the constituents are used. The same product can also be obtained in shorter time, but in decreased quantity, by carrying out the reaction at  $40-50^{\circ}$ .

*The Yellow Modification.*—This modification can be obtained by very gradual dilution with water of an alcoholic solution of the ordinary red variety. It has also been observed in certain preparations on dilution of the original condensation mixture, but in this state it rapidly passes into the red, chromotropic form (Found: C = 75.8; H = 6.9; N = 6.3.  $C_{19}H_{19}O_2N, C_9H_{11}ON$  requires C = 76.0; H = 6.8; N = 6.3 per cent.).

#### *4'-Dimethylamino-2-hydroxydistyryl Ketone.*

This ketone is exceedingly difficult to obtain in the free state, as it very tenaciously retains traces of solvent. It can be best prepared by heating the alcohol additive product for four hours at  $100^{\circ}$  or by triturating the benzene additive product with dry ether. Various other methods, such as recrystallisation from ethyl acetoacetate or precipitation of an ethyl acetate solution with heptane, also produce comparatively pure specimens of the hydroxy-ketone, although not entirely free from solvent. From the alcohol additive product it is obtained as a dull crimson powder melting with violent decomposition at  $154^{\circ}$ . From the benzene additive product, a light brick-red powder is formed, whereas from ethyl acetoacetate it crystallises in tiny, brilliant scarlet crystals. Black nodules giving a red streak are obtained from ethyl acetate solution by means of heptane. These different varieties show a distinct variation in activity; thus, whereas the free compound from ethyl acetoacetate readily unites in alcoholic solution with *p*-dimethylaminobenzaldehyde, the black modification, under similar conditions, does not react (Found: in product from alcohol, N = 4.79; in product from ethyl acetoacetate, N = 4.83; in product from ethyl acetate, C = 77.4; H = 6.8.  $C_{19}H_{19}O_2N$  requires C = 77.8; H = 6.5; N = 4.78 per cent.).

The ketone dissolves in concentrated sulphuric acid with a deep red colour. On warming with concentrated hydrochloric acid, a red solution first forms, which rapidly changes to greenish-yellow. On gradual dilution of this solution with water, very pronounced colour phenomena are observed, the solution first becoming emerald green, then intensely violet, and finally deep indigo-blue. These colour phenomena, which are undoubtedly associated with the formation of benzopyrylium salts, are at present under investigation.

The *acetyl* derivative is readily prepared by warming the hydroxy-ketone with acetic anhydride for two hours and pouring the dark green solution into ice-water. On careful neutralisation with dilute alkali, the acetyl compound is precipitated and is finally purified by crystallisation from acetone. It forms well-defined, bright-red prisms melting at  $153^{\circ}$ , and differs essentially from the free hydroxy-ketone, no longer possessing the power of forming additive compounds with either solvents or aldehydes (Found:  $\lambda = 4.32$ .  $C_{21}H_{21}O_3N$  requires  $N = 4.18$  per cent.).

*o*-Methoxystyryl Methyl Ketone,  $OMe \cdot C_6H_4 \cdot CH : CH \cdot COMe$ .

This ketone was prepared with the intention of condensing it with *p*-dimethylaminobenzaldehyde to form 4'-dimethylamino-methoxydistyryl ketone. Harries (*Ber.*, 1891, **24**, 3180) failed to obtain this compound, but we have found that it may readily be prepared either by direct methylation of *o*-hydroxystyryl methyl ketone with methyl sulphate in aqueous alkaline solution or by condensing *o*-methoxybenzaldehyde with acetone according to Clausen's method. It forms pale yellow leaflets, m. p.  $50^{\circ}$ , b. p.  $84^{\circ}/10$  mm. The *oxime* melts at  $127^{\circ}$  (Found:  $N = 7.35$ .  $C_{11}H_{13}O_2N$  requires  $N = 7.34$  per cent.).

4'-Dimethylamino-2-methoxydistyryl Ketone,  
 $OMe \cdot C_6H_4 \cdot CH : CH \cdot CO \cdot CH : CH \cdot C_6H_4 \cdot NMe_2$ .

This compound could not be prepared either by condensation of *o*-methoxystyryl methyl ketone with *p*-dimethylaminobenzaldehyde or by direct methylation of 4'-dimethylamino-2-hydroxydistyryl ketone under ordinary conditions. It was ultimately obtained, however, in good yield by carrying out the methylation in acetone solution. 18.5 Grams of the benzene additive product, dissolved in the minimum quantity of hot acetone, were treated with 25 c.c. of 10 per cent. sodium hydroxide solution and 8.3 grams (1 mol.) of methyl sulphate added in one lot. The mixture was heated for five minutes and then diluted with water to 500 c.c., when orange

nodules gradually separated. The substance crystallises from absolute alcohol in beautiful bright-red prisms melting at  $95-96^{\circ}$ . It is moderately soluble in most organic solvents and, as in the case of the acetyl derivative, it separates from these without solvent addenda. Although the ether cannot be induced to unite with either *p*-dimethylaminobenzaldehyde or salicylaldehyde, it combines readily with polynitro-hydrocarbons to yield similar additive products to those obtained from the parent substance. It dissolves in both concentrated sulphuric acid and hydrochloric acid with a red colour, which becomes green on dilution, but the intense colour changes exhibited by the parent substance do not occur.

*The Yellow Modification.*—On rapid recrystallisation from hot ethyl acetate, the ether is obtained in long, pale yellow needles having the same m. p. as the red form (Found:  $N = 4.55$ ,  $C_{20}H_{21}O_2N$  requires  $N = 4.56$  per cent.).

*Additive Products of 4'-Dimethylamino-2-hydroxydistyryl Ketone.*

The general methods employed for the preparation of the additive compounds are:

(1) When the addendum is a molecule of a solvent, one of the other additive products (the benzene or chloroform compounds were generally employed) is crystallised from the required solvent, the process being repeated where necessary.

(2) Where the required addendum is a solid substance, the necessary proportions of each component are dissolved together in the minimum quantity of hot ethyl alcohol and the solution left to crystallise.

Unless otherwise stated, the melting point is the same as that of the free ketone.

*Ethyl Alcohol.*— $C_{19}H_{19}O_2N, C_2H_6O$ . This compound crystallises as large, purplish-black aggregates of leafy prisms, with a brick-red streak (Found:  $N = 4.08$ . Calc.,  $N = 4.13$  per cent.).

*Ethyl Acetate.*— $C_{19}H_{19}O_2N, \frac{1}{2}C_4H_8O_2$ , steely black, glistening crystalline mass (Found:  $N = 4.19$ . Calc.,  $N = 4.17$  per cent.).

*Benzene.*— $C_{19}H_{19}O_2N, C_6H_6$ . To obtain this compound it is necessary to crystallise the hydroxy-ketone slowly from a dilute benzene solution. It consists of well-formed, almost black, tapering prisms (Found:  $N = 3.73$ . Calc.,  $N = 3.78$  per cent.).

The compound  $C_{19}H_{19}O_2N, \frac{1}{2}C_6H_6$ , which forms a puce-coloured, crystalline powder, is obtained by boiling the *p*-dimethylaminobenzaldehyde additive compound with benzene (Found:  $C = 79.2$ ;  $H = 6.8$ . Calc.,  $C = 79.5$ ;  $H = 6.6$  per cent.).

*Chloroform.*— $C_{19}H_{19}O_2N, CHCl_3$ .—*Red form.*—Bright red leaflets

with a faint green lustre. This is the isomeride usually obtained from chloroform, in which, however, it is only sparingly soluble (Found : N = 3.43. Calc., N = 3.41 per cent.).

*Blue form*.—This modification consists of small indigo-blue crystals, and is obtained by rapidly precipitating, with vigorous scratching, a solution of the hydroxy-ketone in alcohol and chloroform, with light petroleum. It turns bright red at about 100° and reverts to the red modification without change in weight when exposed to chloroform vapour (Found : N = 3.48. Calc., N = 3.41 per cent.).

*m-Dinitrobenzene*.— $C_{13}H_{19}O_2N, C_6H_4(NO_2)_2$ , reddish-violet prisms, m. p. 121—122° (Found : N = 9.10. Calc., N = 9.11 per cent.).

*s-Trinitrobenzene*.— $C_{13}H_{19}O_2N, 2C_6H_3(NO_2)_3$ , almost black needles giving a maroon-coloured streak. M. p. 180° (Found : N = 13.68. Calc., N = 13.64 per cent.).

*2:4-Dinitrotoluene*.— $C_{13}H_{19}O_2N, C_7H_6(NO_2)_2$ , reddish-violet prisms, m. p. 120—121° (Found : N = 8.5. Calc., N = 8.8 per cent.).

*2:4:6-Trinitrotoluene*.— $C_{13}H_{19}O_2N, 2C_7H_5(NO_2)_3$ , soft, reddish-brown aggregates, m. p. 132° (Found : N = 13.07. Calc., N = 13.1 per cent.).

*p-Benzoquinone*.— $C_{13}H_{19}O_2N, C_6H_4O_2$ , small, greenish-black needles with a violet-black streak. It softens at 118° and melts completely at 144—145° (Found : C = 74.8; H = 6.1. Calc., C = 74.8; H = 5.7 per cent.).

*Acetic Acid-Benzene*.— $2C_{13}H_{19}O_2N, \frac{1}{2}C_6H_5, \frac{1}{2}C_2H_4O_2$ . This compound is prepared by recrystallising the benzene additive product from benzene containing 20 per cent. of glacial acetic acid. The additive complex separates from the dark emerald-green solution in glistening, indigo-blue prisms (Found : C = 76.8; H = 6.8; N = 4.45. Calc., C = 76.9; H = 6.6; N = 4.3 per cent.).

*Phenol*.— $C_{13}H_{19}O_2N, C_6H_5 \cdot OH$ . This substance is formed by crystallising a solution of the components from a mixture of absolute alcohol and light petroleum. It forms large, well-defined, bluish-black, rhombic prisms, red in transmitted light, and gives a dull red streak. The melting point is indefinite, 120—140°, according to the rate of heating (Found : C = 77.5; H = 6.6. Calc., C = 77.6; H = 6.5 per cent.).

*Phenanthrene*.— $C_{13}H_{19}O_2N, \frac{1}{2}C_{14}H_{10}$ , emerald green prisms with greenish-black streak. M. p. 122° (Found : C = 81.3; H = 6.4. Calc., C = 81.6; H = 6.3 per cent.).

*Fluorene*.— $C_{13}H_{19}O_2N, \frac{1}{2}C_{13}H_{10}$ . This product is precipitated from the alcoholic solution by means of light petroleum and vigorous scratching. It forms bright green crystals with a violet-black

streak. M. p.  $126^{\circ}$  (Found: C = 81.3; H = 6.5. Calc., C = 81.4; H = 6.4 per cent.).

*Fluorene + Methyl Alcohol.*— $C_{19}H_{19}O_2N, \frac{1}{2}C_{13}H_{10}, CH_3 \cdot OH$ . The compound is obtained by evaporating an ethyl acetate solution of the solid components to dryness and recrystallising the residue from methyl alcohol. It forms beautiful, dark-red prisms softening at  $85^{\circ}$  and finally melting at  $127^{\circ}$  (Found: C = 77.7; H = 7.0. Calc., C = 77.9; H = 6.9 per cent.).

*Carbazole.*— $C_{19}H_{19}O_2N, C_{12}H_9N$ , crimson crystals melting at  $146^{\circ}$  (Found: N = 6.13. Calc., N = 6.08 per cent.).

*p-Dimethylaminobenzaldehyde.*— $C_{19}H_{19}O_2N, C_8H_{11}ON$ . This compound, which is readily prepared by the general method, melts at  $143^{\circ}$  and is identical in every respect with that already described.

*Anisaldehyde.*— $C_{19}H_{19}O_2N, \frac{1}{2}C_8H_8O_2$ , dark purplish-black plates with unsharp melting point,  $150$ – $154^{\circ}$ , and the same violent decomposition as the free ketone (Found: N = 4.1. Calc., N = 3.9 per cent.).

*Salicylaldehyde.*— $C_{19}H_{19}O_2N, \frac{1}{2}C_7H_6O_2$ . This additive product is obtained by employing the aldehyde as solvent and allowing the solute to crystallise out. It forms small, deep-red prisms softening at  $100^{\circ}$  and melting finally at  $135^{\circ}$  (Found: C = 75.9; H = 6.5. Calc., C = 76.2; H = 6.2 per cent.).

*Salicylaldehyde-Sodium Complex.*—When molecular proportions of the hydroxy-ketone and salicylaldehyde are dissolved in absolute alcohol and one molecular proportion of a concentrated solution of sodium hydroxide is added, a red solid rapidly separates. By crystallisation from an alcohol-light petroleum solution, the compound is obtained as a very characteristic mass of felted, orange needles which melt at  $200^{\circ}$ . Analysis of this compound, which contains from 2–4 per cent. of sodium, does not reveal any very exact stoichiometric relationship between metal, ketone, and aldehyde, although the sodium content agrees comparatively well with that of a compound of the formula  $C_{19}H_{18}O_2NNa, \frac{1}{2}C_7H_6O_2$ . Repeated recrystallisation from the above solvent mixture brings about a gradual decrease in the sodium content, a progressive lowering of the melting point also being observed.

If absolute alcohol alone is employed as crystallising medium, well-formed, brick-red prisms which melt sharply at  $196^{\circ}$  are obtained. Further recrystallisation of these from absolute alcohol produces no depression in the melting point.

The compound is insoluble in water and is readily decomposed by boiling dilute alcohol, the free ketone being regenerated (Found: in the prismatic material, Na = 3.6; N = 3.74.  $C_{19}H_{18}O_2NNa, \frac{1}{2}C_7H_6O_2$  requires Na = 3.2; N = 3.84 per cent.).

*Benzophenone*.— $C_{19}H_{19}O_2, \frac{1}{2}C_{13}H_{10}O$ , dark red crystals with a distinct blue reflex. M. p. 137–143° (Found: C = 76.5; H = 6.8. Calc., C = 76.7; H = 6.9 per cent.).

As it was thought that possibly the sodium of the salicylaldehyde additive product had replaced the hydrogen of the phenolic hydroxyl group of the aldehyde, similar experiments were carried out with benzophenone in place of salicylaldehyde. After the addition of the alkali, the mixture rapidly solidified to a crimson mass of felted needles, which were first recrystallised from absolute alcohol and then from a mixture of alcohol and light petroleum. The product forms soft masses of felted orange needles, very similar in appearance to the salicylaldehyde-sodium additive product. It melts at 197°, which is almost the same temperature as the m. p. of the salicylaldehyde product. Results of analysis indicate that the sodium content approximates to one atom, calculated for  $C_{19}H_{18}O_2NNa, C_{13}H_{10}O$  (Found: Na = 4.9; N = 3.39. Calc., Na = 5.7; N = 3.36 per cent.). Owing to the great difficulty of purification, it seems almost impossible to get concordant results with different specimens, as the sodium content can vary within wide limits, and this noticeably influences the character of the product. It would seem to be definitely established, however, that we are dealing here with a novel type of compound, which we hope to investigate in detail, and also the effect of other metals.

Curiously enough, no additive products could be obtained with aaphthalene, anthracene, or *s*-trinitroanisole. Compounds, which were not further investigated, were formed with *l*-pinene, aniline, pyridine,  $\beta$ -naphthylamine, and numerous other substances.

#### *Additive Products of 4'-Dimethylamino-2-methoxydistyryl Ketone.*

*m*-Dinitrobenzene.— $C_{20}H_{21}O_2N, C_6H_4(NO_2)_2$ , small, dull-red, prismatic needles, m. p. 78° (Found: N = 8.9. Calc., N = 8.85 per cent.).

*s*-Trinitrobenzene.— $C_{20}H_{21}O_2N, 2C_6H_3(NO_2)_3$ , reddish-purple needles with characteristic bronze reflex. M. p. 148° (Found: N = 13.5. Calc., N = 13.4 per cent.).

#### *Fission of Substituted Styryl Methyl Ketones.*

*o*-Hydroxystyryl Methyl Ketone (Harries, *Ber.*, 1891, **24**, 3180).—Four grams of the ketone, dissolved in 12.5 c.c. of absolute alcohol, were treated with 4 c.c. (2 mols.) of 50 per cent. sodium hydroxide solution. After two days 1.1 grams of the sodium salt of 2:2'-dihydroxydistyryl ketone were isolated. The salt was decomposed and the free ketone identified by its reactions and by the melting



point after admixture of a specimen prepared according to Decker and Felsler's method (*loc. cit.*).

*p*-Dimethylaminostyryl Methyl Ketone.—From this substance, proceeding in an analogous manner, *pp'*-tetramethyldiaminodistyryl ketone, m. p. 193°, was isolated; it was identified by the melting point of its mixture with a specimen prepared according to Sachs and Lewin (*Ber.*, 1902, **35**, 3576).

*pp'*-Dimethoxydistyryl Ketone from *o*-Hydroxystyryl Methyl Ketone and Anisaldehyde.—Four grams (1 mol.) of *o*-hydroxystyryl methyl ketone and 6.2 grams (2 mols.) of anisaldehyde, dissolved in the minimum quantity of absolute alcohol, were treated with 7 c.c. of a 50 per cent. solution of sodium hydroxide (3 mols.). After five days, 1.4 grams of almost colourless leaflets were filtered off and identified as the above compound by comparison and by the melting point of its mixture with a specimen obtained by Baeyer and Villiger's method (*Ber.*, 1902, **35**, 1191). It is interesting to note that, starting from *p*-methoxystyryl methyl ketone and salicylaldehyde, only resinous matter is produced. Similar results were obtained from *p*-methoxystyryl methyl ketone itself in presence of alkali.

*pp'*-Tetramethyldiaminodistyryl Ketone from *o*-Hydroxystyryl Methyl Ketone and *p*-Dimethylaminobenzaldehyde.—Sixteen grams of *o*-hydroxystyryl methyl ketone (1 mol.) and 15 grams of the aldehyde (1 mol.) were dissolved in 170 c.c. of absolute alcohol, and 80 c.c. of 10 per cent. aqueous sodium hydroxide (2 mols.) added. The mixture was kept for eight days at room temperature in cold weather. The red needles which had then separated were filtered off, and after crystallisation from alcohol-acetone mixture identified by the melting point and by analysis as *pp'*-tetramethyldiaminodistyryl ketone; the yield was 5 grams (Found: C = 78.5; H = 7.4; N = 8.7. Calc., C = 78.7; H = 7.5; N = 8.6 per cent.).

*pp'*-Tetramethyldiaminodistyryl Ketone from the Additive Compound of 4'-Dimethylamino-2-hydroxydistyryl Ketone and *p*-Dimethylaminobenzaldehyde.—A saturated alcoholic solution containing 4 grams of the additive compound was mixed with 2 c.c. of 50 per cent. sodium hydroxide. After six days, 1.5 grams of a mixture of *pp'*-tetramethyldiaminodistyryl ketone and a small quantity of the salicylaldehyde-sodium complex of the hydroxy-ketone were isolated.

#### *Condensation of p*-Dimethylaminostyryl Methyl Ketone with Salicylaldehyde.

This condensation was carried out in the hope of arriving at a more convenient method for the preparation of the hydroxy-ketone.

The reaction proved, however, to be very slow and was complicated by the slight solubility of the reactants. A considerable quantity of tar was invariably produced, from which only small quantities of the hydroxy-ketone melting at  $154^{\circ}$  were isolated, together with *pp'*-tetramethyldiaminodistyryl ketone.

In conclusion, we wish to express our appreciation of the interest taken in this work by Professor E. C. C. Baly, F.R.S., and to thank him for placing his spectrophotometer at our disposal. We also desire to acknowledge our indebtedness to the Advisory Council for Scientific and Industrial Research for a grant which has enabled this research to be undertaken.

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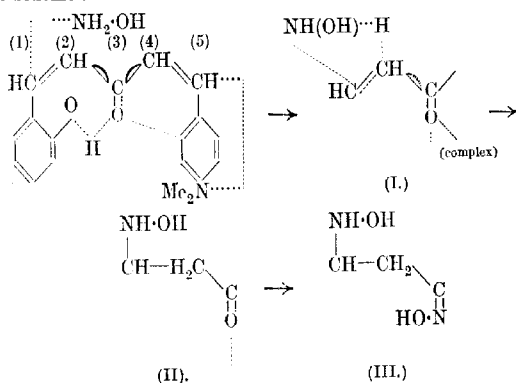
CLXXVIII.—*The Reactivity of Doubly-conjugated Unsaturated Ketones. Part II. The Action of Hydroxylamine, Semicarbazide, and Phenylhydrazine on 4'-Dimethylamino-2-hydroxydistyryl Ketone and its Methyl Ether.*

By ISIDOR MORRIS HEILBRON and JOHANNES SYBRANDT BUCK.

It has been shown in the preceding paper that the high degree of reactivity exhibited by 4'-dimethylamino-2-hydroxydistyryl ketone may be satisfactorily explained by assuming inner complex formation involving the carbonyl oxygen atom and the hydroxyl group, the effect of this being to enhance the free residual affinity of the external carbon atom of the conjugated system included in the complex. In the present paper, further evidence is adduced strongly supporting this hypothesis.

*Action of Hydroxylamine.*—By the action of hydroxylamine hydrochloride upon the hydroxy-ketone in presence of excess of calcium carbonate in the cold, a bright red, labile additive product (I), analogous to the solvates already described, can be isolated. This additive compound very readily loses its hydroxylamine addendum, with formation of the free ketone. If, however, more vigorous methods are employed, such as heating the reactants in concentrated alkaline solution for a short time, in place of the labile additive product, the true hydroxylamino-derivative (II) is

produced in the form of almost colourless needles melting at  $218^{\circ}$ . Finally, an hydroxylamino-oxime (III) can be prepared by the action of hydroxylamine acetate on the ketone in the cold, but whereas the first two substances are rapidly prepared, this compound requires several days for its formation. With the methyl ether, on the other hand, only an hydroxylamino-oxime is produced. It is thus evident that the reaction takes place in successive stages, the first being labile addition by means of subsidiary valence linkings, followed by the strengthening of the partial linkings, finally resulting in the disruption of the double bond. Once this has taken place, the doubly conjugated system has ceased to exist, and, with it, the anomalous behaviour of the carbonyl group also vanishes, and consequently an oxime of the hydroxylamino-compound is obtained. It is likewise assumed that the reaction with hydroxylamine acetate follows the same course, as illustrated by the scheme:



*Action of Semicarbazide.*—The action of this base upon the hydroxy-ketone in presence of pyridine or of semicarbazide acetate itself results in the direct formation of a semicarbazido-semicarbazone, no intermediate compounds having been isolated. During the course of this investigation an interesting paper by Auwers has appeared (*Ber.*, 1921, **54**, [B], 987) in which it is pointed out that the conclusions arrived at by Rupe and his collaborators (*Ber.*, 1903, **36**, 1903; 1907, **40**, 4764), that it is only in the aliphatic group that semicarbazido-semicarbazones are obtainable, must be modified. Auwers, starting from phenyl propenyl ketone, *p*-anisyl propenyl ketone, and *p*-methoxy-*o*-tolyl propenyl ketone, readily obtained semicarbazido-semicarbazones, and concluded that whereas ketones of the type (A), probably owing to their spatial configura-

ion, could only form semicarbazones, ketones of the type (B) examined by him, where the inhibiting influence of the phenyl group was removed, were not so restricted.

(A)  $C_6H_5 \cdot CH:CH \cdot COR$  (B)  $C_6H_5 \cdot CO \cdot CH:CHR$  ( $R$  = aliphatic group).

It is evident, however, from the above, that even compounds containing the ethylenic double bond adjacent to the phenyl group can, under certain conditions, react to yield semicarbazido-semicarbazones. Such a condition would be the strengthening of the necessary subsidiary valencies, which effect occurs, according to our postulate, in 4'-dimethylamino-2-hydroxydistyryl ketone. That, however, the addition of semicarbazide to an ethylenic linking under normal conditions takes place with more difficulty than the addition of hydroxylamine is illustrated by the action of 4'-dimethylamino-2-methoxydistyryl ketone, which only forms a simple semicarbazone. We regard this as a direct proof both of the presence of increased free valency on carbon atom C (1) and that the carbonyl group of the hydroxy-ketone remains inoperative until the complex partial valency system has been fundamentally altered by addition at the double bond.

*Action of Phenylhydrazine.*—A phenylhydrazone is obtained by the action of this base on either the hydroxy-ketone or its methyl ether. That, however, this is in no way contrary to the views just expressed is indicated by the fact that the reaction only takes place in presence of excess of pyridine, and that the phenylhydrazone contains, especially in the case of the hydroxy-ketone, one molecule of pyridine firmly attached. It is evident that the pyridine first forms a "solvate" with the ketone, analogous to the action of hydroxylamine in the formation of the hydroxylamine additive product, and that this occasions a rupture of the ring system, which then reacts to yield the phenylhydrazone-pyridine compound in the ordinary manner. Numerous experiments were carried out with the object of obtaining phenylhydrazine derivatives in the absence of pyridine, but without success, as oils which could not be purified invariably separated out. There can, however, be little doubt that such oils actually contained the phenylhydrazino-additive product analogous to the hydroxylamino-compound.

#### EXPERIMENTAL.

*Additive Product of 4'-Dimethylamino-2-hydroxydistyryl Ketone with Hydroxylamine,*  $OH \cdot C_6H_4 \cdot CH:CH \cdot CO \cdot CH:CH \cdot C_6H_4 \cdot NMe_2 \cdot NH_2 \cdot OH$ .

2.8 Grams of the ketone (benzene additive product) were treated in alcoholic solution with 1.1 grams of an aqueous solution of

hydroxylamine hydrochloride, and the mixture, after being neutralised with powdered calcium carbonate, was immediately filtered. On dilution with water, the additive product rapidly separated as bright scarlet flocks, from which the hydroxylamine addendum was easily removed by keeping over concentrated sulphuric acid (Found: on immediate analysis,  $N = 8.4$ .  $C_{19}H_{19}O_2N.NH_2.OH$  requires  $N = 8.6$  per cent. Found: after two days in exsiccator,  $N = 4.7$ .  $C_{19}H_{19}O_2N$  requires  $N = 4.8$  per cent.).

*Hydroxylamino-derivative of 4'-Dimethylamino-2-hydroxydistyryl Ketone.*

8.4 Grams of the ketone-chloroform product, dissolved in 15.0 c.c. of 30 per cent. potassium hydroxide solution (4 mols.), were treated with 5.5 grams of hydroxylamine hydrochloride dissolved in 40 c.c. of water, and 20 c.c. of alcohol added to the mixture. The whole was boiled for a few minutes, when the solution changed colour, becoming orange-yellow. The hydroxylamino-compound rapidly separated and was purified by repeated crystallisation from absolute alcohol. It forms almost colourless needles, melting with decomposition at  $218^\circ$  (rapid heating). It is somewhat sparingly soluble in most organic solvents, and is slowly decomposed on boiling with hydrochloric acid or aqueous alkali (Found:  $C = 69.6$ ;  $H = 6.9$ ;  $N = 8.5$ .  $C_{19}H_{22}O_3N_2$  requires  $C = 69.9$ ;  $H = 6.8$ ;  $N = 8.6$  per cent.).

*Hydroxylamino-derivative of 4'-Dimethylamino-2-hydroxydistyryl Ketoxime.*

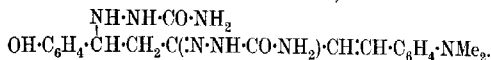
8.2 Grams of the ketone-chloroform product, dissolved in 50 c.c. of alcohol, were treated with 3 mols. of hydroxylamine acetate. The mixture was allowed to stand for three days, and the hydroxylamino-oxime precipitated by dilution with water. The dark tarry product was repeatedly crystallised from alcohol, after decoloration with animal charcoal. It forms pale yellow, silky leaves, which darken above  $200^\circ$  and finally melt with decomposition at  $212^\circ$  (Found:  $C = 66.7$ ;  $H = 7.0$ ;  $N = 12.3$ .  $C_{19}H_{23}O_3N_3$  requires  $C = 66.9$ ;  $H = 6.7$ ;  $N = 12.3$  per cent.).

*Hydroxylamino-derivative of 4'-Dimethylamino-2-methoxydistyryl Ketoxime.*

2.8 Grams of hydroxylamine hydrochloride (4 mols.), dissolved in the minimum quantity of water, were added to a solution of

3.1 grams of the methyl ether dissolved in 15 c.c. of pyridine. The mixture was kept for five days, and then diluted largely with water, when a yellow, oily mass was precipitated. After recrystallisation from a mixture of alcohol and pyridine, it was obtained in glistening, colourless needles melting at  $214^{\circ}$ . This compound may also be obtained by an analogous method to that employed in the preparation of the hydroxylamino-oxime of the hydroxyketone, a less favourable yield, however, being obtained (Found: C = 67.3; H = 7.3; N = 11.9.  $C_{20}H_{25}O_3N_3$  requires C = 67.6; H = 7.1; N = 11.8 per cent.).

*Semicarbazide Derivative of 4'-Dimethylamino-2-hydroxydistyryl Ketone Semicarbazone,*



4.0 Grams of the ketone (chloroform additive product), dissolved in 20 c.c. of pyridine, were mixed with 5.0 grams of semicarbazide hydrochloride dissolved in 15 c.c. of water, and 15 c.c. of alcohol were added in order to form a homogenous solution. After the mixture had been kept for two days, the flocculent, slightly red precipitate of the semicarbazide-semicarbazone was filtered off, and recrystallised from a mixture of aniline and amyl alcohol. It forms an almost colourless powder, melting at  $218^{\circ}$ , which is very sparingly soluble in most organic solvents, but is somewhat soluble in aqueous pyridine and readily soluble in warm aniline. This substance has also been prepared by the usual method with semicarbazide acetate (Found: C = 59.0; H = 6.9; N = 22.8.  $C_{21}H_{27}O_3N_4$  requires C = 59.3; H = 6.4; N = 23.1 per cent.).

*Semicarbazone of 4'-Dimethylamino-2-methoxydistyryl Ketone.*

Three grams of an alcoholic solution of the methyl ether were mixed with an excess of semicarbazide acetate. After standing for two days, the precipitated semicarbazone was filtered off, and freed from unchanged methyl ether by washing with boiling alcohol. The semicarbazone, after recrystallisation from chloroform, forms brilliant yellow leaves melting at  $213^{\circ}$  (Found: N = 15.3.  $C_{21}H_{24}O_2N_4$  requires N = 15.4 per cent.).

*Pyridine Additive Product of 4'-Dimethylamino-2-hydroxydistyryl Ketone Phenylhydrazone.*

16.4 Grams of the chloroform additive product of the ketone were dissolved in 50 c.c. of pyridine, and 17 grams (3 mols.) of

phenylhydrazine hydrochloride added. The mixture was heated for thirty minutes on the water-bath, after which it was kept at the ordinary temperature. On cooling, the whole solidified to a yellow mass, which was redissolved in a small quantity of pyridine. Addition of ethyl acetate caused the separation of a small amount of a yellow substance readily soluble in water, but this was not further investigated. The ethyl acetate was driven off and the residue allowed to crystallise after the addition of alcohol. Ten grams of the hydrazone were thus obtained as a yellow, crystalline mass melting at  $141^{\circ}$ . On repeated crystallisation from benzene, the melting point gradually rises, which effect must be due to the gradual removal of the pyridine, as the substance melting at  $141^{\circ}$  can again be obtained by one recrystallisation from alcoholic pyridine. No accurate analytical results could be obtained for the compound of higher m. p., but it was indicated that the pyridine addendum was being partly replaced by benzene. None of the compounds gave the Knorr pyrazoline reaction (Found: C = 78.0; H = 6.8; N = 12.1.  $C_{25}H_{25}ON_3$  requires C = 77.9; H = 6.5; N = 12.2 per cent.).

*Phenylhydrazone of 4'-Dimethylamino-2-methoxydistyryl Ketone.*

3.1 Grams of the methyl ether were dissolved in 15 c.c. of pyridine and treated with 4.3 grams (3 mols.) of phenylhydrazine hydrochloride. After heating for one hour on the water-bath, a pale yellow oil, which rapidly solidified on standing, separated out, and was recrystallised from alcohol-pyridine mixture. The phenylhydrazone forms pale yellow clusters, melting at  $127^{\circ}$ , readily soluble in pyridine, but only slightly soluble in alcohol. The results of analysis show this compound to be a pyridine additive product (Found: C = 78.0; H = 7.0.  $C_{26}H_{27}ON_3 \cdot C_5H_5N$  requires C = 78.1; H = 6.7 per cent.). On recrystallising this compound from absolute alcohol, the pyridine is removed. The free phenylhydrazone consists of lemon-yellow prisms melting at  $154^{\circ}$ . This compound, as well as that obtained from the hydroxy-ketone itself, exhibits an intense greenish-yellow fluorescence in dilute solution (Found: N = 10.7.  $C_{26}H_{27}ON_3$  requires N = 10.6 per cent.).

In conclusion, we desire to express our thanks to the Advisory Council for Scientific and Industrial Research for a grant which has enabled this investigation to be undertaken.

CLXXIX.—*Surface Tensions of Salts of the Fatty Acids and their Mixtures.*

By ERIC EVERARD WALKER.

THOSE salts of the fatty acids which are useful soaps lower the surface tension of water to an altogether abnormal extent; a study of the surface tension of soap solutions is therefore of very special interest. The object of the present paper is to examine this property under a variety of conditions and thereby to learn something of the changes which take place in solution when the temperature or concentration is varied or when one soap is wholly or partly replaced by another of the same or a nearly related series.

It was believed that the information so gained would lead to a better understanding of the manner in which different soaps interact in solution to produce an effect on the surface tension which is either greater or less than would be expected from the proportions in which the constituents are present.

The results have to a large extent justified expectations, in that a theory primarily advanced in order to explain the manner in which surface tension varies with temperature, concentration, and the number of carbon atoms, has been found capable of explaining the behaviour of mixed soaps in solution.

*Measurement of Surface Tension.*

The surface tension was measured with a simple form of dropping pipette. It is not claimed that the results obtained are of absolute value, and in fact it was found that different pipettes gave different results. It is, however, well known that the apparent surface tension of soap solutions depends to a very marked extent on the exact conditions under which it is determined. All that can be claimed is that the conditions were carefully standardised so that the results might be of comparative value. The pipette and receiver were completely immersed in a constant-temperature bath, necessitating a simple device outside the water-bath for regulating the rate of flow. This consisted of a U-tube connected with the upper end of the pipette and fitted with a tap on the longer arm. Water was allowed to flow from the longer arm into the shorter at a regulated speed, thus allowing the soap solution to flow out of the pipette at a similar rate.

The required quantity of acid was weighed out, dissolved in alcohol, and neutralised with an alcoholic solution of sodium



hydroxide. This was evaporated, the residue dissolved in water and the solution made up to the required weight. The water used was redistilled and the first and last thirds were rejected. The alcoholic sodium hydroxide solution was made up by dissolving sodium in alcohol redistilled over lime. All concentrations were expressed in terms of the number of grams of acid per 100 grams of solution.

Solutions made up in this way could be kept unchanged for a day or so. If the alcoholic sodium hydroxide solution is made up with ordinary stick sodium hydroxide, progressive rise in the surface tension takes place, noticeable after an hour or so. The effect of keeping solutions made as described is shown in the following table.

*Surface Tension in dynes per cm.*

	Laurate.	Myristate.	Palmitate.
Fresh solution .....	29.2	19.8	19.8
After four hours at 60° .....	29.2	19.7	19.8
After twenty-four hours at 60° .....	29.1	19.5	19.9
After eight days at room temperature ...	29.9	19.7	20.2

The soap solution, which had been kept at the required temperature for fifteen minutes or longer, was drawn up into the pipette, taking care to avoid air bubbles. The regulating U-tube and the receiver were then attached and the apparatus was placed in the water-bath. Five minutes were allowed to elapse before the determination was made, in order that the temperature might become uniform.

The soap solution was then adjusted to the top mark on the pipette, approximately 2 c.c. were run out drop by drop at a rate of 20 drops every minute, the flow being stopped at the first complete drop after the 2 c.c. mark had been passed. The pipette was calibrated to read to 0.01 c.c. between 2.0 c.c. and 2.1 c.c. The volume was then reduced to grams for the purpose of calculation.

Twenty drops every minute was chosen as the rate of flow. A much slower rate has its advantages, especially in the case of soap solutions, but it was considered unsatisfactory in the present instance on account of the tendency of moisture to condense on the jet and drop at high temperatures, and of the probability that unsaturated soaps would interact with the atmosphere.

All surface tensions were calculated with reference to the drop number of water determined with the same pipette, at the same temperature as that used for the determination of the soap solution.

*Effect of Concentration.*

In this manner the surface tensions of several salts of the fatty acids were determined at concentrations varying from 0.005 per

TABLE I.

*Surface Tension at 60° in dynes per cm.*

Concentration.	Laurate.	Myristate.	Palmitate.	Stearate (impure).	Arachidate.	Oleate.
0.005	64.0	64.0	64.2	65.7	—	65.7
0.01	61.3	54.7	42.2	52.0	—	46.9
0.025	54.9	39.2	26.6	32.5	—	28.0
0.05	45.9	26.9	21.85	26.7	65.3	23.75
0.075	41.1	22.5	20.95	24.4	—	22.35
0.1	38.0	21.2	20.5	23.9	61.0	22.55
0.15	—	20.3	19.95	—	—	—
0.2	29.2	20.6	19.85	22.4	56.9	—
0.25	—	21.2	—	—	—	—
0.3	24.5	—	20.7	22.5	—	—
0.4	—	23.9	22.3	—	56.7	—
0.5	21.2	—	—	23.1	—	—
0.75	26.5	—	—	23.1	—	—
1.0	28.3	26.4	23.65	23.6	—	—
1.5	29.3	—	—	—	—	—
2.0	29.4	—	—	—	—	—

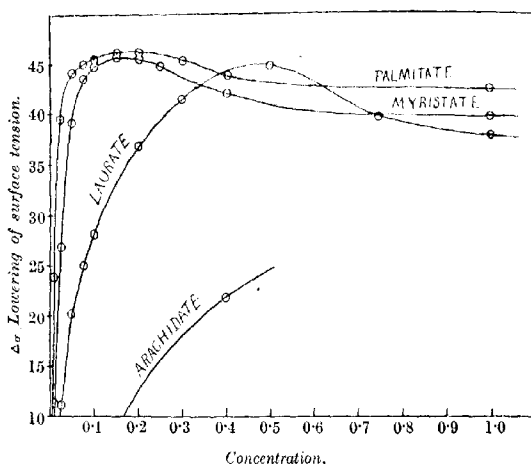
ent. to 1.0 per cent. The standard temperature chosen was 60°. The results (mean values) are given in Table I. In Fig. 1 these results are represented graphically. The concentration is represented by the abscissæ and the *lowering of the surface tension* (water = 60 dynes/cm. at 60°) by the ordinates.

The palmitic acid was impure. It had the correct equivalent, but contained about 7 per cent. of oleic acid and melted at 58–59°. The stearic acid was a commercial sample. It contained only 1.5 per cent. of oleic acid, but about 40 per cent. of palmitic acid. It was, however, suited to the present purpose, since the pure soap is only soluble to the extent of 0.2 per cent. at 60°. The remaining acids were practically pure. With the exception of "stearic acid," however, they all give a good idea of the general trend of the curve. It is interesting to note that this impure soap follows closely the contour of the palmitate curve, although it contains a preponderating proportion of stearate. This will be referred to later in the section on mixtures. The interesting point about these curves is that they tend to rise to a maximum and that this maximum is almost the same for all soaps the solubility of which is great enough to allow the maximum to be reached. This is very suggestive, and indicates that at this point the surface layer of all soaps is similar. Probably it consists of a stable emulsion containing a high percentage of soap.

Using carefully purified materials, the initial part of the curve was redetermined. Special care was taken over these determinations, since it is at these low concentrations that different soaps can best be compared with one another. For instance, it is scarcely

fair to compare a 0.2 per cent. palmitate solution with a 0.2 per cent laurate solution, since the former has reached its maximum while the latter has not. At a concentration of 0.5 per cent., sodium laurate would appear to be more effective than either myristate or palmitate. As the tip of the pipette had been damaged, it was necessary to use a new one, and as this gave different results from the old one, the results are not directly comparable. Two completely

FIG. 1.



independent series of measurements were made, except in the case of sodium arachidate, and the mean values are given in Table II.

TABLE II.

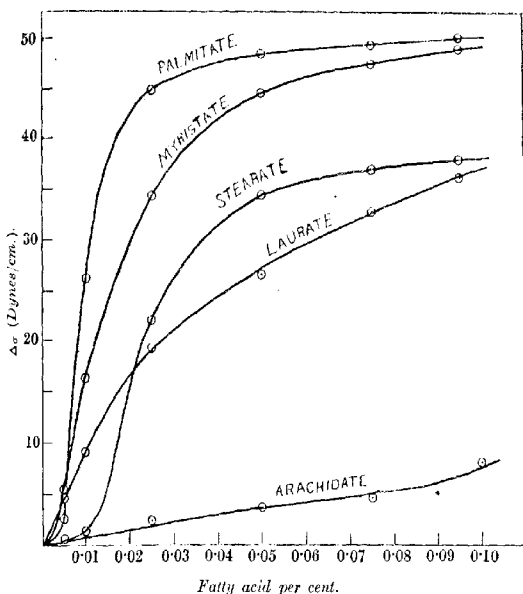
Lowering  $\sigma$ , Surface Tension at 60° in dynes per cm.

Concen- tration.	Water—66.0.				Pipette No. 3.			
	<i>n</i> -Octo- ate.	<i>n</i> -Deco- ate.	Laurate.	Myrist- ate.	Palmit- ate.	Stear- ate.	Arachid- ate.*	Behen- ate.
0.005	—	—	4.7	5.4	2.5	0.6	—	—
0.01	—	—	9.1	16.3	26.1	1.3	—	—
0.025	—	—	19.3	34.3	44.8	22.0	2.3	—
0.05	—	—	26.7	44.6	48.4	34.4	3.6	—
0.075	—	—	32.8	47.5	49.3	36.9	4.6	—
0.1	1.55	6.4	36.2	48.9	50.0	37.7	8.1	1.6

\* Single series of determinations only.

Curves are plotted in Fig. 2. The interesting part about these curves is the first inflection in the early part of the curve, and the significance of this will be considered in the section on theory. It should be pointed out that sodium stearate does not form a clear 0.1 per cent. solution like sodium myristate and laurate; the solution has at 60° a curious opalescent appearance, due, no doubt, to the presence of colloidal particles. Bearing in mind McBain's work

FIG. 2.



on the proportions in which colloidal soap is present in solution, seems probable that this phenomenon may be due to partial hydrolysis.

#### *Effect of Temperature.*

The temperature coefficients of the surface tensions of pure liquids have led to results of great theoretical significance. In the case of solutions and mixtures, however, conditions are much more complex and theory has not made much headway.

Fig. 3 illustrates forcibly the effect of temperature in the case of sodium arachidate. At 60°, it lowers the surface tension only

to a very small extent; at  $90^{\circ}$ , however, the whole contour of the curve is altered and becomes similar to that of sodium stearate at  $60^{\circ}$ .

The full line in the  $60^{\circ}$  curve represents the behaviour of a perfectly fresh solution. The dotted line indicates the surface tension of a solution which has been kept at a temperature of  $60^{\circ}$  for some time and has partly gelatinised.

FIG. 3.

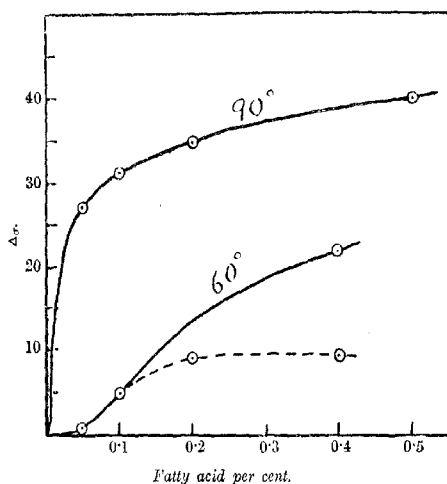


TABLE III.

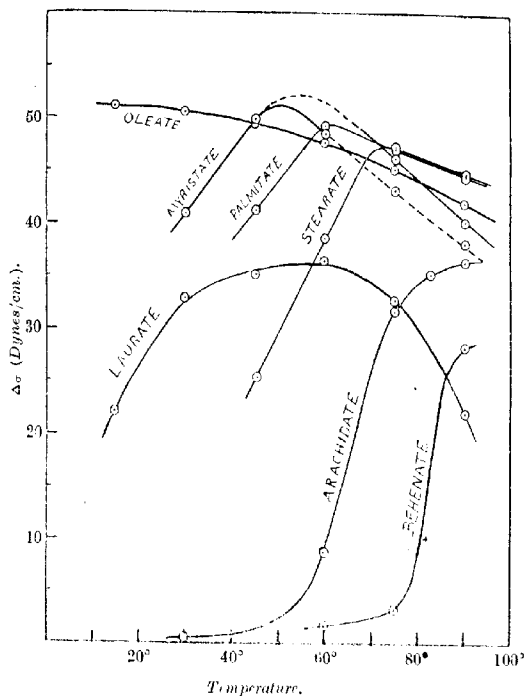
Temperature Curves.—Pipette No. 3.

Temp.	Oleate.	Laurate.	Laurate.	Myrist- ate.	Palmit- ate.	Stear- ate.	Arachid- ate.	Behen- ate.
	0.1%	0.5%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%
15°	51.1	51.8	22.0	—	—	—	—	—
30	50.58	51.55	32.75	41.0	—	—	0.5	—
45	49.4	49.65	35.15	50.0	41.3	25.2	—	—
60	47.7	48.0	36.45	48.5	49.3	38.7	8.6	1.6
75	45.15	45.75	32.75	46.25 (43.25)	47.0	47.2	31.6	3.15
90	42.1	41.9	21.9	40.2 (38.2)	44.4	44.6	36.3	28.2
T = 82.7° 35.1								

In Table III data obtained at various temperatures are recorded, and curves are plotted in Fig. 4. In general, the extent to which the surface tension is lowered increases to a maximum with the temperature, and then decreases. Sodium oleate either shows no

maximum or more probably it is below 15°. In most cases, the temperature at which the maximum occurs rises with the molecular weight, but the behaviour of sodium laurate is exceptional. At a higher concentration (0.5 per cent.), however, the laurate curve becomes almost identical with the 0.1 per cent. oleate curve, and thus falls more or less into its place. Sodium oleate itself is interest-

FIG. 4.



ng, and differs from all the other soaps at 0.1 per cent. concentration in that its efficiency in lowering the surface tension remains high over a wide range of temperature.

#### *Effect of Molecular Weight.*

The manner in which the effect of the salts of the fatty acids on the surface tension of water changes from member to member

TABLE IV.

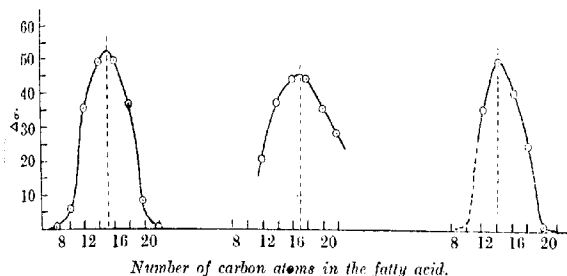
Palmitate and Myristate 60°.				Oleate and Myristate 60°.				Stearate and Laurate 60°.			
% Palmitate.	$\Delta\sigma$ .	Deviation.	% Palmitate.	$\Delta\sigma$ .	Deviation.	% Oleate.	$\Delta\sigma$ .	% Stearate.	$\Delta\sigma$ .	Deviation.	% Stearate.
0	48.93	—	0	47.75	—	0	48.7	0	34.6	—	0
25	49.15	+0.1	25	48.25	+0.1	25	47.75	25	29.3	-7.2	25
50	49.5	+0.1	50	49.1	+0.15	50	47.6	50	30.3	-5.8	50
75	49.6	+0.5	75	49.55	+0.0	75	47.65	75	35.0	-1.8	75
100	49.9	—	100	50.15	—	100	47.7	100	37.55	—	100
Palmitate and Stearate 60°.				Myristate and Arachidate 60°.				Oleate and Laurate 60°.			
% Palmitate.	$\Delta\sigma$ .	Deviation.	% Myristate.	$\Delta\sigma$ .	Deviation.	% Stearate.	$\Delta\sigma$ .	% Oleate.	$\Delta\sigma$ .	Deviation.	% Oleate.
0	39.15	—	0	33.4	—	0	7.4	0	37.0	—	0
25	43.75	+1.9	25	43.9	+5.7	25	25.4	25	45.53	+5.85	25
50	46.0	+1.5	50	46.35	+3.3	50	34.2	50	46.75	+4.35	50
75	48.25	+1.05	75	47.85	+3.65	75	38.15	75	47.4	+2.35	75
100	49.9	—	100	48.6	—	100	39.45	100	47.75	—	100
Oleate and Stearate 60°.				Arachidate and Laurate 60°.				n-Decoate and n-Octoate 60°.			
% Oleate.	$\Delta\sigma$ .	Deviation.	% Arachidate.	$\Delta\sigma$ .	Deviation.	% Palmitate.	$\Delta\sigma$ .	% Decoate.	$\Delta\sigma$ .	Deviation.	% Decoate.
0	38.35	—	0	34.3	—	0	50.3	0	1.55	—	0
25	48.05	+6.2	25	9.6	-18.3	25	44.75	25	2.2	-0.6	25
50	48.05	+5.05	50	9.3	-12.15	50	42.25	50	4.7	+0.7	50
75	48.3	+3.0	75	9.0	-6.0	75	40.85	75	13.6	+8.4	75
100	47.65	—	100	8.6	—	100	39.35	100	6.4	—	100

of the series is remarkable when we consider the gradual way in which most properties change as an homologous series is ascended. Just as in the case of temperature and concentration, the activity of the soap rises to a maximum, after which an increase in the molecular weight is associated with a decrease in the activity of the soap. The curves in Fig. 5 show how the effect on the surface tension varies with the number of carbon atoms under various conditions.

#### Mixed Soaps.

Solutions of 0.1 per cent. strength were made up as usual and the surface tension of these was determined. The solutions were then mixed in various proportions and the surface tension of the mixtures

FIG. 5.



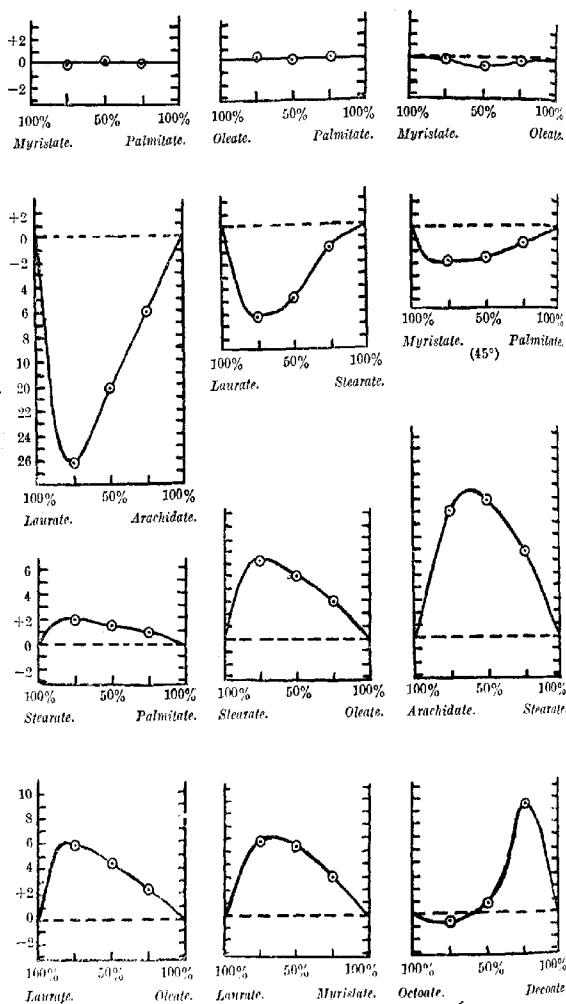
determined. The results are recorded in Table IV. In Fig. 6 the results are represented diagrammatically by plotting the deviations from the "mixture law" against the composition of the solution. If a series of mixtures follows the "mixture law," that is, the surface tension of all mixtures is equal to the weighted mean of that of the constituents, the curve then becomes a horizontal straight line as in the case of palmitate and myristate or palmitate and oleate. The majority of mixtures are, however, represented by curves falling either above or below this hypothetical line.

#### Theoretical.

It has been shown that molecular weight, temperature, and concentration all exert an effect on capillary activity which rises to a maximum and then decreases. From this it would appear that there must be some condition of equilibrium between two forms of soap present in solution, and that if this equilibrium is disturbed, either in one direction or the other, by changes in temperature or



Fig. 6.



concentration (or by substituting another soap of greater or smaller molecular weight), the property of lowering the surface tension (or interfacial tension) will be greatly diminished or will disappear.

These facts can be explained and a foundation for the theory of soap mixtures laid if we regard soap in aqueous solution as containing colloidal aggregates or "micelle" in equilibrium with simpler molecules. This view has long been advocated by McBain, who arrived at this conclusion in order to explain the osmotic behaviour of soap solutions in relation to their electrical conductivity.

It may be assumed with reason that the equilibrium between these colloidal aggregates and the simpler molecules is affected by temperature and concentration in much the same manner as is the equilibrium between complex and simple molecules.

Thus dissociation is promoted by :—

increase in temperature,  
decrease in molecular weight,  
decrease in concentration;

and association is promoted by :—

decrease in temperature,  
increase in molecular weight,  
increase in concentration.

It should be remembered that on account of the lowering of the surface tension the solution is more concentrated in the surface layer. In the case of those soaps lowering the surface tension to a large extent, there must be some circumstance which facilitates the concentration of the soap in the surface layer. This is to be found in the readiness with which they form complex colloidal molecules. According to McBain, there are only immeasurably small quantities of colloidal soap in dilute solutions. At the surface, however, under the influence of high concentration and high pressure, conditions are suitable for the formation of large colloidal aggregates. The lowering of the surface tension tends to hold these at the surface against their osmotic pressure. This osmotic pressure is, however, small and the surface concentration is therefore abnormally great.

To bring this theory into line with facts, we must assume that very large micelle are not so active, weight for weight, in lowering the surface tension of soap solutions as those of moderate size. Therefore, if the size of the colloidal aggregates is increased beyond a certain limit, there is a falling off of efficiency, even although the surface concentration may remain high. Such an assumption is reasonable in view of the fact that the special forces active in the surface layer only penetrate beneath the surface to an extent depending on the range of molecular action (see Parks, *Phil. Mag.*, 1903, [vi], 5, 517). Therefore, when the colloidal particles reach

dimensions which are large in comparison with molecular magnitudes, a falling off in efficiency must necessarily be expected (Lewis claims that emulsions of paraffin in aqueous solution have little or no effect on the interfacial tension. *Phil. Mag.*, 1908, [vi], **15**, 499). Hence we have the following system:—

Small micelle efficient in lowering the surface tension, but difficult to chain to the surface on account of their relatively high osmotic pressure.	$\rightleftharpoons$	Large micelle inefficient in lowering the surface tension, but easy to chain to the surface on account of their relatively low osmotic pressure.
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It may be assumed that the highly efficient soaps, such as palmitate and myristate, are those in which surface concentration and specific activity are so combined as to give a maximum value. Those of lower molecular weight are less efficient because the relatively high osmotic pressure of the small micelle hinders the formation of a high surface concentration. The higher homologues readily form large micelle, which, having a low osmotic pressure, are easily adsorbed in the surface layer. Nevertheless, one would expect that the surface concentration of stearate, arachidate, and behenate would be progressively less than that of palmitate on account of the decreased activity of the larger micelle. There is, however, every reason to suppose that the surface concentration of these soaps is much greater than that of the "nut oil" soaps, which lower the surface tension to a corresponding extent (see p. 1522).

Milner (*Phil. Mag.*, 1907, [vi], **13**, 96) and Lewis (*Phil. Mag.*, 1908, [vi], **15**, 499; 1909, [vi], **17**, 466) examined the relationship between surface tension and surface concentration for a variety of solutions in the light of Gibb's theory. Both authors grafted on to this theory the assumption that the solutions with which they were dealing followed the gas laws, and found that the majority of substances were very much more concentrated in the surface layer than the theory thus modified would lead them to expect. Lewis found that Congo-red was about thirty times and sodium oleate about one hundred times more concentrated in the surface layer than the theory required. McBain's work has proved that the gas laws cannot be applied to such substances in concentrated solution, and their theory was not therefore applicable to these cases, for the concentration is high in the surface layer, even although small in the body of the solution. Lewis explained the apparent discrepancy by assuming that gelatinisation takes place in the surface layer. No special hypothesis is required, however, if McBain's theory of colloidal electrolytes is accepted.

*(a) Relationship between Surface Tension and Concentration.*

When the soap solution is extremely dilute, the concentration in the surface layer will be sufficiently small for the soap to consist mainly of simple molecules. As the concentration is increased, complexes will increase in the surface layer, slowly at first and then with increasing rapidity. The more complexes are formed the smaller will be the work required to be done by surface tension against the osmotic pressure in order to concentrate the soap in the surface layer.

McBain's work has shown that the osmotic pressure rises fairly rapidly with the concentration until a maximum is reached, and that it then falls slightly, thereafter rising much more slowly. As soon as the point is reached at which an increase in concentration is associated with an actual decrease in osmotic pressure, followed by a region in which the osmotic pressure rises slowly with the concentration, a very rapid increase in the surface concentration must necessarily follow. One would therefore expect that the surface concentration would at first increase slowly with the volume concentration and then with increasing rapidity.

These expectations are realised in the early part of the concentration curves (see Fig. 2), and, moreover, this first inflection becomes more marked as the molecular weight (and therefore the tendency to form complexes) increases.

The occurrence of a maximum in the surface-tension curve is explained by the hypothesis that the efficiency of the colloid particles falls off as their size increases, hence the whole form of the concentration curve is in qualitative agreement with the requirements of theory.

The form of McBain's concentration-osmotic pressure curves shows that there are in certain circumstances three concentrations having one and the same osmotic pressure.

Since surface tension is so intimately connected with osmotic pressure, it would not be surprising to find that for one and the same volume concentration there could be more than one surface tension. This appears to be the case for sodium myristate at 75° and 90°. The readings were as follows :—

	Drops per gram.		Drops per gram.
75°	112	90°	84.5
	111.5		84
	94.5		101
	96.5		105
	113		103
	112		103

In another series of five readings for a temperature of 75° and using another pipette, only one high reading was obtained

3 G\* 2

Attempts to obtain either the one reading or the other by approaching the temperature from above or below met with no success. The phenomenon is therefore different from that observed in the case of arachidic acid. Moreover, gelatinisation was not observed and would not be expected at this temperature.

(b) *Temperature.*

The theory is in harmony with the fact that there is an optimum temperature for every soap and that in general this rises as the homologous series is ascended. This optimum temperature appears to have some connexion with the melting point of the acid. It seems not unreasonable to suppose that at the melting points of the acids, the corresponding soaps exist in approximately similar molecular states so far as their tendency to form complexes is concerned.

(c) *Mixed Soaps.*

There are three ways in which mixed soaps might be expected to behave in dilute solution.

(1) The soaps might act independently, each constituent lowering the surface tension to an extent corresponding with its individual concentration. In this case, owing to the form of the concentration curves, almost any mixture would be much more efficient than a single soap, weight for weight. Mixtures would not be expected to behave in this way unless they were very dilute both in solution and *in the surface layer*. It would not, therefore, be in accordance with the theory, and is not, in fact, found to be the case.

(2) The soaps might form mixed complexes at the surface having properties intermediate between those of the constituents. If these mixed complexes in the surface layer contained the constituents in the same proportions in which they were present in solution, one might expect that the resultant lowering of the surface tension would be approximately the weighted mean of those of the constituents at the combined concentration of the mixed soaps, that is, the mixed soaps would apparently follow the so-called mixture law. There is, however, no reason to suppose that two different soaps would be adsorbed to the same extent in the surface layer either in the form of mixed complexes or otherwise. Hence it is only in the case of mixtures of soaps lowering the surface tension to approximately the same extent that one would expect the mixture law to be followed.

Thus, for instance, the three pairs:—

Myristate and palmitate at 60°.

Oleate and myristate     "     "

Oleate and palmitate     "     "

follow very closely the mixture law (see Fig. 6). At 45°, however, palmitate lowers the surface tension to a much smaller extent than myristate. Accordingly, at this temperature the mixture law is not followed. Laurate and stearate also lower the surface tension to about the same extent; they are, however, very dissimilar in other respects, the form of the concentration curves being very different. Mixtures of these two soaps do not follow the mixture law. It is, therefore, reasonable to suppose that in these circumstances the complexes formed do not possess properties intermediate between those of the two constituents.

(3) The majority of soap mixtures come under the third head, the capillary activity of the mixtures being related in no simple manner to that of the constituents. Having shown that the mixture law holds fairly closely under certain conditions, the simplest plan is to regard all mixtures not following this law as lowering the surface tension by so much more or so much less than the law would indicate. The behaviour of mixtures is therefore represented graphically on this plan in Fig. 6. From what has been said in the preceding paragraph one would expect that that soap which is most readily absorbed in the surface layer would have the predominant effect; in what follows such a soap will be called a dominant soap. As a general rule this soap will be the one which lowers the surface tension to the largest extent. This is not, however, necessarily the case, since the lowering of the surface tension depends on *two* factors :—

(1) Concentration in the surface layer.

(2) Specific activity of the soap in the surface layer.

If the dominant soap lowers the surface tension more than the other, mixtures of the two will have a *lower* surface tension than the mixture law would indicate. If, on the other hand, the dominant soap lowers the surface tension to a smaller extent than that with which it is mixed, the reverse is to be expected. All the mixtures hitherto examined, with the exception of laurate and stearate, conform to this rule if the soaps are regarded as dominating each other in the order of the following empirical list :—

- |    |                             |
|----|-----------------------------|
| 1. | { Palmitate-C <sub>16</sub> |
|    | { Oleate                    |
| 2. |                             |
| 3. | Stearate-C <sub>18</sub>    |
| 4. | Arachidate-C <sub>20</sub>  |
|    | Behenate-C <sub>22</sub>    |
| 5. | Myristate-C <sub>14</sub>   |
| 6. | Laurate-C <sub>12</sub>     |
| 7. | n-Decoate-C <sub>10</sub>   |
| 8. | n-Octoate-C <sub>8</sub>    |

This list, although empirical in a sense, is nevertheless in harmony with the theory put forward in this paper, which requires that the adsorptive powers (or the tendency of the soap to concentrate at the surface) shall increase to a maximum as the homologous series is ascended and then decrease. A very interesting example of the way in which one soap can almost completely dominate another in the surface layer is the case of laurate and arachidate. Arachidate lowers the surface tension by 8.6 dynes, and laurate by 34.3 dynes, nevertheless, when 75 per cent. of the arachidate is replaced by laurate the extent to which the mixture lowers the surface tension is only increased to 9.6 dynes. With regard to the form of the curves in Fig. 6, theory indicates that the greatest deviation from the mixture law should occur when a small quantity of the dominant soap is mixed with a large quantity of the other, that is, the peak of the curve should always be displaced towards that end of the diagram corresponding with low concentrations of the dominant soap. This is so in nearly every case investigated, even in the somewhat exceptional case of laurate and stearate. Mixtures of decoate and octoate are the only exceptions in this respect.

The exceptional behaviour of mixtures of laurate and stearate indicates that the principles enunciated cannot be applied absolutely rigidly. They cover perhaps the most important aspect of the problem, but when the difference in the adsorptive power is large and the difference between the capillary activities is small, as in the case of this pair, then these effects may be masked by secondary changes. Evidence of such changes is also found in the case of mixtures of oleate and stearate, and decoate and octoate, where certain mixtures lower the surface tension to a *greater* extent than either of the constituents.

#### *Summary of Results.*

The activity of various salts of the fatty acids in lowering the surface tension of water has been examined at various concentrations and temperatures, and the manner in which this activity varies with changing conditions has been explained on the basis of McBain's theory of soap solutions.

Only one additional hypothesis has been found to be necessary, and this is to the effect that the lowering of the surface tension is not solely proportional to the concentration in the surface layer, but that it depends also on the size of the colloidal particles. McBain's theory, together with this hypothesis, suffices to explain the following facts.

(1) Soaps lower the surface tension of the water in which they are dissolved to an altogether abnormal extent.

(2) In an homologous series of soaps the power of lowering the surface tension first rises with increasing molecular weight and then falls after passing through a maximum.

(3) In general, the property of lowering the surface tension rises to a maximum as the temperature is increased and then falls off.

(4) The property of lowering the surface tension increases slowly with the concentration at extreme dilution, then rises rapidly and after passing through a maximum decreases again.

(5) When soaps are mixed in solution, the extent to which they lower the surface tension cannot be determined from the properties of the constituents. By means of the theory it is possible, as a rule, to determine whether a mixture of any two soaps will lower the surface tension more or less than the weighted mean of the constituents.

In conclusion, the author desires to acknowledge the permission of Messrs. Joseph Crosfield and Sons, Ltd., to publish this paper.

KIRRI,  
INDIA.

[Received, May 12th, 1921.]

### CLXXX.—*ortho*-Chlorodinitrotoluenes. Part III. Bases derived from 2-Chloro-4 : 5-dinitrotoluene.

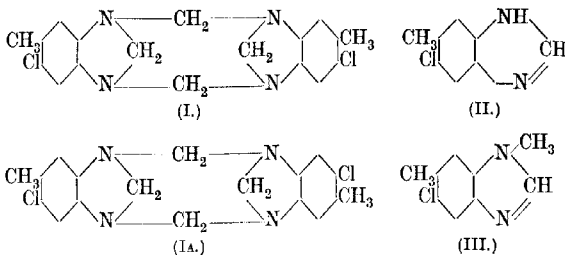
By GILBERT T. MORGAN and WILLIAM ARTHUR PERCIVAL  
CHALLENGOR.

2-CHLORO-4 : 5-DINITROTOLUENE, described in Part I of this communication (T., 1920, **117**, 786), gives rise to 6-chloro-3 : 4-tolylene-diamine, an exceptionally stable *ortho*-diamine, which, when starting from *o*-toluidine, can be prepared by methods giving an overall yield of about 33 per cent. On this account the base can with advantage be substituted for *o*-phenylenediamine in those condensations where a diamine is employed in the characterisation of  $\alpha$ -diketones or *ortho*-quinones. With these dicarbonyl compounds the new diamine gives rise to well-defined, readily crystallisable derivatives.

As an example of condensation with monocarbonyl derivatives, the interactions of 6-chloro-3 : 4-tolylene-diamine and formaldehyde were examined in neutral and in acid solutions. Under the former of these conditions two dimeric hydrolysable condensation products were obtained, each of which had the composition corresponding



with *tetramethylenebis-6-chloro-3:4-tolylenediamine*. The possibility of isomerism is indicated by the following formulæ I and IA.



In acid solution, the formaldehyde condensation takes a different course, the monomeric non-hydrolysable *5-chloro-1:6-dimethylbenzimidazole* (III) being produced. This amidine is also obtained by condensing *6-chloro-3N-methyl-3:4-tolylenediamine* with formic acid, an alternative method of preparation which demonstrates its constitution.

The amidine condensation proceeds normally also with *6-chloro-3:4-tolylenediamine* and its *3N*-phenyl derivative, the constitution of the resulting methenyl compounds being represented respectively by formulæ II and VI.

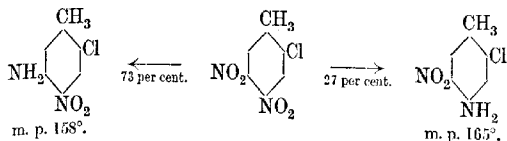
*Action of Ammonia on 2-Chloro-4:5-dinitrotoluene. A Correction.*

Attention has been directed in Part I of this communication (T., 1920, **117**, footnote, p. 789) to a discrepancy in the melting points of two different preparations of *6-chloro-4-nitro-m-toluidine*. The product obtained by the action of alcoholic ammonia on *2-chloro-4:5-dinitrotoluene* melted at  $144^{\circ}$ , whereas the substance previously obtained by nitrating *6-chloro-aceto-m-toluidide* melted at  $158-159^{\circ}$  (B.A.S.F., D.R.-P. 226772).

It has now been found that the more fusible product is a mixture of approximately 73 per cent. of *6-chloro-4-nitro-m-toluidine* and 27 per cent. of *6-chloro-3-nitro-p-toluidine* (m. p.  $165^{\circ}$ ). This mixture retains its composition on repeated crystallisation from alcohol, petroleum (b. p.  $80-90^{\circ}$ ), or glacial acetic acid, and has the appearance of being a homogeneous substance. A similar difficultly separable mixture of dinitrotoluidines has been observed by Körner and Contardi (*Atti R. Accad. Lincei*, 1916, [v], **25**, ii, 339).

This observation is of some theoretical interest as illustrating Kenner's theory of the replacement of nitro-groups by aminoradicles (T., 1914, **105**, 2717; 1920, **117**, 852). In the present

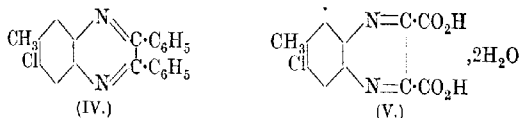
instance the two nitro-groups are alternatively removed in the following proportions.



## EXPERIMENTAL.

6-Chloro-3:4-tolylenediamine was readily prepared by the following series of reactions. Redistilled *o*-toluidine, nitrated in concentrated sulphuric acid, gave a mixture of 4- and 6-nitro-*o*-toluidines, which was separated by fractional crystallisation of the hydrochlorides; the yield of 4-nitro-*o*-toluidine was 75 per cent., whilst about 2—5 per cent. of the 6-nitro-isomeride was isolated from the more soluble fraction (Noelting and Collin, *Ber.*, 1884, 7, 265; Green and Lawson, *T.*, 1891, 59, 1013). Application of the Sandmeyer reaction to the chief product gave an 80 per cent. yield of 2-chloro-4-nitrotoluene. Nitration of the chloro-derivative furnished 2-chloro-4:5-dinitrotoluene (85 per cent.) and upwards of 4 per cent. of 2-chloro-4:6-dinitrotoluene. The dinitro-compound was converted quantitatively into crude 6-chloro-4-nitro-*m*-toluidine (yield 97 per cent.) by alcoholic ammonia and this base reduced to 6-chloro-3:4-tolylenediamine (yield 85 per cent.) with fine dust and dilute alcohol containing ammonium chloride (*ibid.* 1920, 117, 786).

Condensation of 6-Chloro-3 : 4-tolylenediamine with  $\alpha$ -Diketones and ortho-Quinones. 6(7)-Chloro-2 : 3-diphenyl-7(6)-methylquin-  
oxaline (Formula IV).

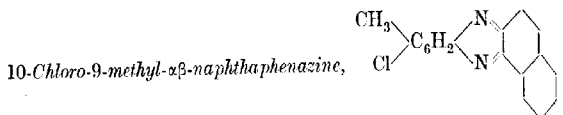


Three grams of benzil and 2 grams of 6-chloro-3:4-tolylenediamine dissolved in 30 c.c. of glacial acetic acid were heated at 100° for fifteen minutes, when white needles separated, the solution becoming nearly solid when cold. The product, when crystallised from alcohol and glacial acetic acid, separated in colourless needles melting at 148.5° and developing a red coloration with concentrated sulphuric acid (Found: N = 8.52.  $C_{21}H_{15}N_2Cl$  requires N = 8.47 per cent.).

This quinoxaline derivative dissolved readily in hot petroleum (b. p. 80–100°), and was very soluble in benzene or chloroform.

*6(7)-Chloro-7(6)-methylquinoxaline-2:3-dicarboxylic Acid*  
(Formula V).

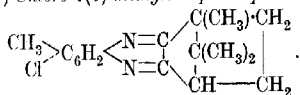
Potassium dihydroxytartrate (3.6 grams) was added slowly to a boiling solution of 6-chloro-3:4-tolylenediamine (2 grams) in 160 c.c. of water and 40 c.c. of alcohol. The faintly red solution was then acidified with concentrated hydrochloric acid, when a pale green, crystalline precipitate separated. This product was redissolved on boiling after the addition to the mother-liquor of 200 c.c. of water. The pale greenish-yellow needles deposited from solution after filtering off a green by-product were recrystallised from water containing a small amount of alcohol and hydrochloric acid, when the substance melted at 173° with decomposition (Found: N = 9.41; H<sub>2</sub>O = 12.05. C<sub>11</sub>H<sub>7</sub>O<sub>4</sub>N<sub>2</sub>Cl.2H<sub>2</sub>O requires N = 9.26; H<sub>2</sub>O = 11.90 per cent.). The hydrated acid lost water at 110°, the anhydrous residue melting at 165°. Concentrated sulphuric acid developed an orange coloration.



Two grams of the diamine dissolved in 200 c.c. of 50 per cent. acetic acid were added slowly with vigorous shaking to a solution of 2 grams of  $\beta$ -naphthaquinone in 140 c.c. of 75 per cent. acetic acid. The gelatinous precipitate which separated was crystallised from benzene, when the azine separated in brownish-yellow crystals with purple reflex, or from glacial acetic acid, when the product was obtained in brown needles melting at 213° (Found: N = 10.28. C<sub>17</sub>H<sub>11</sub>N<sub>2</sub>Cl requires N = 10.06 per cent.).

This azine developed an intense purple coloration with concentrated sulphuric acid.

*6(7)-Chloro-7(6)-methylcamphanoquinoxaline,*



Equal weights of camphorquinone and 6-chloro-3:4-tolylenediamine were boiled together in 15 per cent. alcoholic solution for a few minutes. The product precipitated by water was purified by

peated crystallisation from dilute alcohol. This quinoxaline formed colourless needles melting at  $124^{\circ}$  and developing with concentrated sulphuric acid a yellow coloration (Found: N = 9.92.  $C_{17}H_{13}N_2Cl$  requires N = 9.77 per cent.; 0.4177 in 12.8 c.c. of alcoholic solution in a 1-dm. tube gave  $\alpha_D + 0.91^{\circ}$ , whence  $[\alpha]_D + 7.9^{\circ}$ , corresponding with  $[M]_D + 80^{\circ}$ .

*Interaction of 6-Chloro-3:4-tolylenediamine and Formaldehyde.*

*1. In Neutral Solution.*

Six c.c. of 40 per cent. formaldehyde solution, rendered neutral with two drops of *N*-sodium hydroxide, were added slowly to a solution of 3 grams of 6-chloro-3:4-tolylenediamine in 20 c.c. of boiling alcohol. After two or three minutes a precipitate appeared and spread throughout the liquid. This solid product, crystallised repeatedly from benzene, gave colourless, diamond-shaped crystals melting at  $225^{\circ}$ , the yield being 82 per cent. (Found: N = 15.65.  $C_{17}H_{13}N_2Cl$  requires N = 15.52 per cent. Ebullioscopic determination in benzene gave  $M = 365.1$ , 369.6.  $C_{18}H_{14}N_4Cl_2$  requires  $M = 612$ ). These results confirm the dimeric formula I or IA for the substance.

*Tetramethylenebis-2-chloro-4:5-diaminotoluene* has the properties of a Schiff base and regenerates formaldehyde on warming with acids. The alcoholic mother-liquors from the foregoing Schiff base were diluted with water and the solution was extracted with ether. The residual oil from the ethereal extract deposited slowly a colourless solid which, after crystallisation from water, sublimed at  $170^{\circ}$  and melted completely at  $175^{\circ}$ . The compound, which is isomeric with the preceding substance, also undergoes hydrolysis with aqueous acids, liberating formaldehyde (Found: N = 15.54. Theory requires N = 15.52 per cent.).

*2. In Acid Solution. 5-Chloro-1:6-dimethylbenziminazole*  
(Formula III).

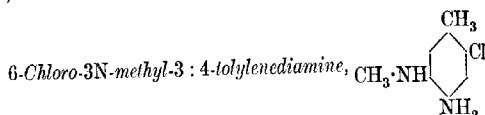
Concentrated hydrochloric acid (7 c.c.) and 40 per cent. formaldehyde solution (10 c.c.) were added successively to 5 grams of 6-chloro-3:4-tolylenediamine dissolved in 30 c.c. of alcohol; the hydrochloride of the diamine was precipitated and then redissolved and the resulting brown solution heated under reflux for thirty minutes. The cooled solution was rendered alkaline with dilute aqueous sodium hydroxide and the oil extracted with ether. The ethereal extract dried over potassium carbonate was distilled until a pale yellow oil passed over at  $340\text{--}345^{\circ}$ , which became solid

and was then crystallised from benzene and light petroleum, when white needles were obtained melting at  $154^{\circ}$  (Found : N = 15.52.  $C_9H_9N_2Cl$  requires N = 15.52 per cent. Ebullioscopic determination in benzene gave  $M = 203, 192$ .  $C_9H_9N_2Cl$  requires  $M = 180.6$ ). The *benziminazole* dissolved readily in alcohol or chloroform, but was almost insoluble in ether or light petroleum.

5-Chloro-6-methylbenziminazole (Formula II).

6-Chloro-3:4-tolylendiamine (5 grams) was heated for two hours at  $100^{\circ}$  with 5 c.c. of 80 per cent. formic acid; the base dissolved to a brown solution, which solidified on cooling. This product, which was the formate of the methenyl base, yielded the amidine on treatment with aqueous ammonia. The amidine, when crystallised from hot water, separated in colourless needles melting at  $189^{\circ}$  (Found : N = 16.85.  $C_8H_7N_2Cl$  requires N = 16.82 per cent.).

The *amidine* dissolved readily in ether, alcohol, acetone, or hot water, but was almost insoluble in cold chloroform. The *formate*, prepared by adding formic acid to an ethereal solution of the base, separated from water in white, filamentous needles melting at  $135^{\circ}$  (Found : N = 13.23.  $C_8H_9O_2N_2Cl$  requires N = 13.13 per cent.).



This compound was prepared by digesting 2-chloro-4:5-dinitro-toluene with alcoholic methylamine (this vol., p. 189) and by reducing the resulting 6-chloro-4-nitro-*N*-methyl-*m*-toluidine (4 grams) with 5 grams of 80 per cent. zinc dust in 100 c.c. of boiling alcohol (75 per cent.) containing 0.8 gram of ammonium chloride. This reduction was completed by refluxing for one hour with the further addition of 4 grams of zinc dust. The diamine separated slowly in pink needles on pouring the cold filtered solution into 500 c.c. of water containing 5 grams of sodium hydroxide (yield 75 per cent.). Owing to its great solubility in ordinary solvents the base was purified by sublimation in a vacuum, when colourless arborescent needles were obtained melting at  $60^{\circ}$  (Found : N = 16.55.  $C_8H_{11}N_2Cl$  requires N = 16.43 per cent.).

When heated above its subliming point, this diamine became red and then changed into a dark bluish-purple decomposition product, sparingly soluble in water and dissolving readily in alcohol or mineral acids.

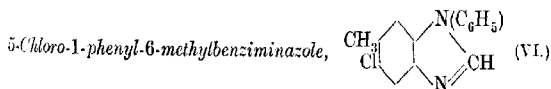
*Action of Formic Acid on 6-Chloro-3N-methyl-3:4-tolylenediamine.*—Equal parts of the diamine and concentrated formic acid were refluxed for two hours and the solution was rendered alkaline with ammonia. The solid product, which was somewhat discoloured, was crystallised repeatedly from benzene and identified as 5-chloro-1:6-dimethylbenziminazole (m. p. 154°).

*Action of Formaldehyde on 6-Chloro-3N-methyl-3:4-tolylenediamine.*—*In Neutral Solution.*—The addition of 6 c.c. of 40 per cent. formaldehyde neutralised with two drops of *N*-sodium hydroxide to 3 grams of the diamine in 20 c.c. of alcohol led to a condensation product, which separated as a non-solidifying oil on dilution with water and was extracted with ether. As this oily material was not crystallisable from organic media, it was distilled, when at 140° a yellow oil was obtained which set to a yellow solid. This product, crystallised repeatedly from benzene, proved to be 5-chloro-1:6-dimethylbenziminazole, melting at 154° (formula III).

*In Acid Solution.*—To 3 grams of the diamine dissolved in 15 c.c. of alcohol were added successively 4.2 c.c. of concentrated hydrochloric acid and 6 c.c. of formaldehyde solution; the hydrochloride of the base separated and redissolved, the mixture becoming appreciably warm. After refluxing for thirty minutes, the mixture was rendered alkaline with potassium hydroxide, extracted with ether, and the extract dried over potassium carbonate. Dry hydrogen chloride was passed into the dried ethereal solution, when a tarry impurity separated and subsequently a crystalline dihydrochloride. This salt, washed with cold chloroform to remove coloured impurities, crystallised from the hot solvent in colourless needles melting with decomposition at 140° (Found: N = 10.49.  $C_{10}H_{12}N_2Cl_3$  requires N = 10.40 per cent.).

The base could not be liberated by ammonia, but when freed with potassium hydroxide and crystallised from ether or petroleum b. p. 80—100°, was obtained from the latter in colourless, rhomboidal plates melting at 100° (Found: N = 13.20, 13.16.  $C_{10}H_{13}N_2Cl_2H_2O$  requires N = 13.06 per cent.).

These results correspond with the following formulæ for base and dihydrochloride respectively:  $CH_3 \cdot C_6H_2Cl \cdot [N(CH_3)]_2 \cdot CH_2 \cdot H_2O$  and  $CH_3 \cdot C_6H_2Cl \cdot [N(CH_3)]_2 \cdot CH_2 \cdot 2HCl$ .



2-Chloro-4:5-dinitrotoluene was converted successively into 1-chloro-4-nitro-*N*-phenyl-*m*-toluidine and 6-chloro-3*N*-phenyl-3:4-tolylenediamine (this vol., p. 190). This diamine was refluxed

for an hour with an equal weight of concentrated formic acid. The solution, which solidified on cooling, was rendered ammoniacal, the solid product was crystallised first from alcohol with addition of animal charcoal and then repeatedly from petroleum (b. p. 80–90°). The amidine separated in colourless needles melting at 100° (Found : N = 11.81.  $C_{14}H_{11}N_2Cl$  requires N = 11.55 per cent.).

[With F. R. JONES.]

*6-Chloro-4-nitro-m-toluidine*, m. p. 158–159°.

*Preparation of 6-Chloro-m-toluidine.*

1. From 2-Chloro-5:6-dinitrotoluene.—This dinitro-compound was converted successively into 6-chloro-3-nitro-*o*-toluidine and 2-chloro-5-nitrotoluene (Morgan and Drew, T., 1920, **117**, 787). This nitro-compound on reduction yielded 6-chloro-*m*-toluidine (m. p. 85°).

2. From *p*-Toluenesulphon-*o*-toluidine.—*o*-Toluidine was converted into its *p*-toluenesulphonyl derivative (m. p. 108°); 20 grams of the latter suspended in 50 c.c. of water at 60° were treated with 20 c.c. of nitric acid (D 1.4), the mixture being stirred at 60–70° for three to four hours. The product recrystallised from alcohol was *p*-toluenesulphon-5-nitro-*o*-toluidide (m. p. 172°). If the foregoing temperatures are exceeded, further nitration occurs, so that after hydrolysis the product contains 3:5-dinitro-*o*-toluidine (m. p. 208°) and a small amount of 3-nitro-*o*-toluidine. The mono-nitrated amide (10 grams) was dissolved in 60 c.c. of concentrated sulphuric acid on the water-bath. The cooled solution, when poured into 200 c.c. of water and rendered alkaline, yielded 5-nitro-*o*-toluidine, which was recrystallised from hot water (m. p. 130°). This base, when put through the Sandmeyer reaction with cuprous chloride, gave 2-chloro-5-nitrotoluene, which on reduction yielded 6-chloro-*m*-toluidine.

*Nitration of 6-Chloro-aceto-m-toluidide.*

6-Chloro-*m*-toluidine (2 parts) was heated for one hour with 1 part of acetic anhydride mixed with an equal weight of glacial acetic acid. The acetyl derivative, when crystallised from petroleum, melted at 92°. Five grams of this acetyl compound were added slowly to a mixture of 4 c.c. of nitric acid (D 1.40) and the same volume of fuming nitric acid (D 1.50). After sixteen hours, the solution, when poured into water, gave an oil solidifying very quickly to a golden-yellow solid, which, after crystallisation from

alcohol, melted at  $113^{\circ}$ . One gram of this acetyl compound was dissolved in 6–8 c.c. of concentrated sulphuric acid by raising the temperature cautiously to  $130^{\circ}$ . After being maintained for a few minutes at this temperature, the solution was cooled and poured into 250 c.c. of water, when an orange-yellow nitro-base was obtained, the precipitation being completed by the addition of ammonia. After crystallisation from alcohol 6-chloro-4-nitro-*m*-toluidine separated in yellow prisms melting at  $158$ – $159^{\circ}$ .

*Mixed Melting Points of 6-Chloro-4-nitro-m-toluidine and 6-Chloro-3-nitro-p-toluidine.*

6-Chloro-3-nitro-*p*-toluidine (m. p.  $165^{\circ}$ ) was prepared by the following processes: nitration of *o*-toluidine, conversion of 4-nitro-*o*-toluidine into 2-chloro-4-nitrotoluene, reduction to 6-chloro-*p*-toluidine, nitration of 6-chloro-aceto-*p*-toluidide, and hydrolysis of the nitro-product.

Mixed melting points were taken with mixtures of the two isomeric bases with the following results:

Percentage of the more fusible base (158.5°) in the mixture	100	90	80	70	60	50	40	30	20	10	0
Melting point of the mixture	158.5°	152.5°	148°	143.5°	140.5°	139.5°	139°	141°	147.5°	156°	164.5°

It is evident that the preparation melting at  $144^{\circ}$  recorded in Part I of this communication (*loc. cit.*) is a mixture consisting approximately of 73 per cent. of 6-chloro-4-nitro-*m*-toluidine and 27 per cent. of 6-chloro-3-nitro-*p*-toluidine. This conclusion was confirmed by taking mixed melting points of a mixture of the pure bases in the foregoing proportions with the preparation melting at  $144^{\circ}$ ; the observed melting points were  $143.5$ – $146^{\circ}$  and  $144$ – $146^{\circ}$ . This constancy of melting point indicated identity of composition in the two mixtures, whether obtained by mixing the pure isomerides or by acting on 2-chloro-4:5-dinitrotoluene with alcoholic ammonia.

6-Chloro-4-nitro-*m*-toluidine from 6-chloro-*m*-toluidine was methylated and phenylated under the experimental conditions described in Part II of the communication (this vol., p. 189–190). The melting points of the products, 6-chloro-4-nitro-*N*-methyl-*m*-toluidine and 6-chloro-4-nitro-*N*-phenyl-*m*-toluidine, were  $126^{\circ}$  and  $96^{\circ}$  respectively, showing that these compounds are identical with the chief products of the action of methylamine and aniline on 2-chloro-4:5-dinitrotoluene.

The authors desire to express their thanks to the Advisory



Council of the Department of Scientific and Industrial Research for grants which have partly defrayed the expenses of this investigation.

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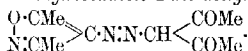
CLXXXI.—*Non-aromatic Diazonium Salts. Part VII.*  
*The Diazo-reaction in the isoOxazole Series.*

By GILBERT T. MORGAN and HENRY BURGESS.

4-AMINO-3:5-DIMETHYLISOXAZOLE has been shown recently (this vol., p. 697) to give rise to diazonium salts comparable in stability with those derived from aniline and its homologues. The reactions of 3:5-dimethylisooxazole-4-diazonium chloride have now been examined further with the object of ascertaining to what extent the isooxazolediazonium salts can be used as synthetic agents.

Non-aromatic azo-derivatives are obtainable by coupling the diazonium salt with the  $\beta$ -diketones and  $\beta$ -ketonic esters.

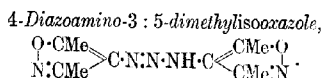
3:5-Dimethylisooxazole-4-azo-acetylacetone,



One gram of 4-amino-3:5-dimethylisooxazole in 5 c.c. of concentrated hydrochloric acid was cooled in a freezing mixture and diazotised by adding slowly 0.7 gram of sodium nitrite; the diazo-solution was then added to one gram of acetylacetone in 8 c.c. of 12 per cent. aqueous sodium hydroxide. The precipitation of the lemon-yellow azo-derivative was completed by salting out (yield 80 per cent.). After several crystallisations from alcohol, the compound was obtained in well-defined, yellowish-orange, hexagonal prisms melting at 115.5–116.5° (Found: N = 19.05.  $\text{C}_{10}\text{H}_{13}\text{O}_3\text{N}_3$  requires N = 18.83 per cent.).

3:5-Dimethylisooxazole-4-azo-acetylacetone was very soluble in cold aqueous caustic alkalis, hydrochloric acid, glacial acetic acid, and the ordinary organic media excepting light petroleum; it dissolved sparingly in hot water, but was insoluble in cold water. On warming, it reduced Fehling's solution and gave neither colour

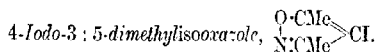
reaction with ferric chloride nor copper salt with neutral copper acetate.



A diazo-solution prepared as above from one molecular proportion of the aminoisooxazole hydrochloride was added to an aqueous solution of the base (1 mol.) and sodium acetate (5 mols.). The pale brown product, precipitated completely by adding sodium chloride, was crystallised from a mixture of equal parts of acetone and light petroleum, from which solution the diazoamine first separated in colourless, transparent, hexagonal prisms which did not change if removed from the solvent. If left in contact with the mother-liquor, however, for several days, these prismatic crystals changed into small, opaque, white octahedra. Both forms of the diazoamine melted at 179–180° (Found: N = 29.93; C = 51.05; H = 5.70.  $\text{C}_{10}\text{H}_{13}\text{O}_2\text{N}_5$  requires N = 29.77; C = 51.02; H = 5.57 per cent.).

4-Diazoamino-3 : 5-dimethylisooxazole was soluble in the ordinary organic media excepting light petroleum; it dissolved in hot water or in aqueous caustic alkalis, and was reprecipitated from the latter by acids. It was very stable towards hydrolytic agents, and was not decomposed by cold concentrated hydrochloric acid.

*isoDiazo-reaction.*—A cold solution of 3 : 5-dimethylisooxazole-4-diazonium chloride (0.7 gram) was added slowly to 7 grams of sodium hydroxide in 6 c.c. of water. A reddish-pink precipitate appeared, but redissolved to a deep red solution, the temperature rising to 20°. This solution coupled with alkaline  $\beta$ -naphthol only in the course of several hours, but if first cautiously acidified it coupled immediately. The alkaline solution slowly lost its coupling power and on passing carbon dioxide into this solution a brown oil separated, which no longer coupled even after acidifying.

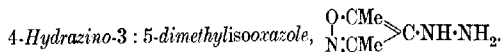


As the chloro- and bromo-isooxazoles appeared to be oily substances like the 4-triazo-compound (*loc. cit.*, p. 782), the iodo-derivative was prepared in order to demonstrate the replacement of the diazo-group by a halogen. The diazonium sulphate from 1 gram of aminodimethylisooxazole was added to 7 grams of potassium iodide in 10 c.c. of water. Rapid effervescence occurred

and a reddish-brown oil separated having an odour like that of iodoform, but more lachrymatory. After two hours, the mixture was distilled in steam and the distillate freed from iodine by sodium hydroxide.

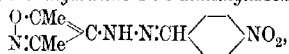
4-Iodo-3:5-dimethylisooxazole, when purified by repeated distillation in steam, separated in very pale yellow needles melting at 52.5–54° (Found: I = 57.47.  $C_5H_6ONi$  requires I = 56.93 per cent.).

This iodo-derivative was very soluble in ether, acetone, chloroform, or benzene, but less soluble in alcohol or hot water. It was extremely volatile, distilling in the vapour of acetone, and when left for four days over sulphuric acid about one-third of the preparation had volatilised. It was accompanied by a small amount of less volatile by-product separating in golden-yellow needles melting at 181–182° and containing no iodine. When pure, 4-iodo-3:5-dimethylisooxazole is only faintly odorous, although distinctly irritant to the eyes.



To a cold solution of 3:5-dimethylisooxazole-4-diazonium chloride prepared from 2 grams of the base were added 11 grams of stannous chloride dissolved in 8 c.c. of concentrated hydrochloric acid. A yellow, frothy precipitate, which first appeared, redissolved on stirring to a yellow solution, which was cooled to  $-5^\circ$ . The solution was made alkaline with sodium hydroxide and the hydrazine extracted with chloroform. This extract, when dried over sodium sulphate and evaporated at the ordinary temperature, left a pale green solid melting at 65–72° and having a strong odour resembling that of dimethylisooxazole. In subsequent experiments the viscous residue from the chloroform was dissolved in alcohol and warmed on the water-bath with *p*-nitrobenzaldehyde (1 mol.). The resulting hydrazone separated as a brick-red precipitate and was crystallised from alcohol in garnet-red, highly refractive prisms having a tough resinous fracture and melting at 183–184° (Found: N = 21.33.  $C_{12}H_{12}O_3N_4$  requires N = 21.53 per cent.).

4-*p*-Nitrobenzylidenchydrazino-3:5-dimethylisooxazole,



was soluble in ether, alcohol, chloroform, benzene, or acetone. A dilute solution of the hydrazone in the last of these solvents assumed an intense greenish-blue colour on the addition of concentrated aqueous sodium hydroxide; this coloration, which is

probably due to the formation of a highly coloured sodium salt of the type  $[\text{C}_6\text{H}_6\text{ON}]\text{NH}\cdot\text{N}\cdot\text{C}\cdot\text{C}_6\text{H}_4\cdot\text{NO}\cdot\text{ONa}$ , is destroyed by acids and even by carbon dioxide or water.

Attempts to replace the diazonium group by ethoxyl or hydroxyl did not lead to the expected result. In the latter case about 20 per cent. of a solid product was obtained crystallising in colourless, transparent plates or lath-like needles melting at  $139\text{--}140^\circ$  (Found:  $\text{N} = 25.49, 25.56$  per cent.). This substance, which contains approximately the same amount of nitrogen as the original aminodimethylisooxazole, was also obtained in an attempt to replace the diazo-complex by a sulphinic group.

#### Summary.

1. The foregoing experiments, in addition to those of the earlier communication (*loc. cit.*), show that the diazonium group, when attached to an isooxazole ring, is replaceable by the halogens and by the triazo-group, but not by hydroxyl, ethoxyl, or sulphinic groups.

2. In alkaline solutions an unstable isodiazo-compound is produced.

3. Reduction of the diazonium chloride leads to an unstable 4-hydrazinodimethylisooxazole.

4. isooxazolediazonium salts couple with bases to form diazo-amino-derivatives and with phenols and  $\beta$ -diketones to yield mixed aliphatic-aromatic and non-aromatic azo-derivatives respectively.

The authors desire to express their thanks to the Advisory Council of the Department of Scientific and Industrial Research for grants which have partly defrayed the expenses of this investigation.

THE CHEMICAL DEPARTMENT,  
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CLXXXII.—*A New Type of Iodine Compound.*

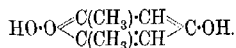
By JOHN NORMAN COLLIE and AMY ADA BEATRICE REILLY.

When dimethylpyrone is boiled with excess of barium hydroxide, the yellow barium salt of diacetylacetone is precipitated. If this salt is suspended in alcohol and treated with iodine, it first dissolves, and on warming a crystalline barium salt separates which does not further react with iodine. The reaction ceases when two atoms of iodine have been added for each atom of barium. Only one-half of the iodine reacts to form barium iodide, the other half reacts with the diacetylacetone, for the barium salt that separates, when treated with dilute acids, gives a compound  $C_7H_7O_3I$  (T., 1900, 77, 1116).

It is difficult to give an explanation how the compound  $C_7H_7O_3I$  is formed from the barium salt of diacetylacetone by the action of iodine.

If all the dimethylpyrone,  $C_7H_8O_2$ , is acted on by the iodine, and converted into  $C_7H_7O_3I$ , the yield should be four times the amount always obtained. Moreover, only half the barium in the barium salt is acted on by the iodine. Therefore the barium salt of diacetylacetone must contain at least two barium atoms in the molecule, and they must be linked differently. The ordinary formula for diacetylacetone,  $CH_3 \cdot CO \cdot CH_2 \cdot CO \cdot CH_2 \cdot CO \cdot CH_3$ , will not allow of any such difference.

The above formula for diacetylacetone also does not agree with some of its physical properties. This was pointed out (T., 1901, 87, 1451). Moreover, other properties and reactions are not satisfactorily explained by the above formula. Amongst organic compounds there is always a tendency to form ring compounds whenever possible, and it may be that diacetylacetone is a ring compound,



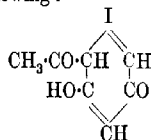
Such a formula would give a barium salt, where the barium atoms would be linked in two different ways, one to the oxygen of the hydroxyl group attached to oxygen, and one to the hydroxyl group attached to carbon. Iodine might only react with the barium replacing the hydrogen of the hydroxyl group attached to the oxygen.

The reaction of iodine with the barium salt of diacetylacetone, moreover, is different from the action of iodine with the sodium salt of acetylacetone, that gives tetra-acetylene. In the reaction producing the compound  $C_7H_7O_3I$  there must be an oxidising

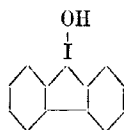
tion. It may be that the barium in the barium salt of diacetylpyrone reacts in the same way as barium hydroxide does with indine, giving a mixture of iodide and hypoiodite, the latter acting as the oxidising agent. But there does not seem to be any simple equation that will explain the formation of the compound  $C_7H_7O_3I$ . Moreover, from its properties and reactions it is no simple derivative either of diacetylacetone or of dimethylpyrone.

It might be iodosodimethylpyrone,  $O < \begin{smallmatrix} C(CH_3)=CH \\ C(CH_3):C(IO) \end{smallmatrix} > CO$ , but it is not decomposed by sodium hydroxide, and all pyrone compounds are. It might be iodoso-orcinol, but it gives no orcinol reactions. It is neither a hypoiodite nor an iodo-compound. It is a strong acid liberating carbon dioxide from carbonates and forming metallic salts, but the iodine is easily removed as silver iodide when warmed with silver nitrate and nitric acid; it can, however, be boiled with concentrated sodium hydroxide solution without decomposition. Chlorine water does not liberate iodine. From its acid properties it contains either a carboxyl group or an  $-OH$  group. The presence of a carboxyl group is not possible. It gives a monoacetyl derivative, and reacts with two molecules of phenylhydrazine.

The only simple formula that agrees with most of its properties and reactions is the following :



When it dissolves in water the iodine atom becomes quinquevalent, taking up the elements of water. Ring compounds containing iodine are not novel. Mascarelli (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 580; *Gazzetta*, 1908, 38, ii, 619) describes one that is a strong base capable of absorbing carbon dioxide from the air.



Basic.



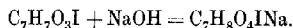
Acid.

That iodine in a ring with four carbon atoms should be basic, and in a ring with five carbon atoms should be acid, is behaviour exactly the reverse of that of nitrogen in pyrrole and pyridine. The remaining reactions of the compound  $C_7H_7O_3I$  are the following :

With an excess of bleaching powder solution it gives a precipitate of calcium carbonate. The amount was estimated, (1) as carbon dioxide (Found:  $C = 14.2$ ), (2) the carbon dioxide absorbed by potassium hydroxide (Found:  $C = 13.5$ ), (3) as precipitated calcium carbonate (Found:  $C = 13.5$ ). Theory for three atoms of carbon  $C = 13.5$  per cent.

When boiled under reflux with very dilute sulphuric acid, it gradually decomposes, giving acetic acid, hydriodic acid, and some substance that chars with concentrated sulphuric acid, and reduces Fehling solution, and also gives a precipitate with phenylhydrazine. The substance, however, does not seem to be a sugar, for it can be extracted slowly by means of ether, but it has not been obtained in a crystalline condition.

When heated with water at  $130-140^\circ$ , the substance  $C_7H_7O_3I$  decomposes almost quantitatively into hydriodic acid, acetic acid, carbon, and water, as follows,  $C_7H_7O_3I + H_2O = HI + CH_3 \cdot CO_2H + 5C + 2H_2O$ ; 0.936 gave 0.198 C, 0.432 HI, 0.202  $CH_3 \cdot CO_2H$ , the theoretical amounts being 0.211 C, 0.450 HI, 0.211  $CH_3 \cdot CO_2H$ . It is not, however, decomposed by boiling water. It is a monobasic acid, for when titrated with  $N/10$ -sodium hydroxide it forms a salt;



The mean of three molecular-weight determinations by the freezing point method gave  $M = 263$ .  $C_7H_7O_3I$  requires  $M = 266$ .

When the substance is boiled with dilute alcohol and sodium amalgam, the iodine is quantitatively removed as sodium iodide, and this is the simplest method of estimating the iodine in the substance and its compounds.

With potassium iodide and a dilute acid, it gives no free iodine. It can be dissolved in warm concentrated sulphuric acid without decomposition, and is reprecipitated on the addition of water, but if a strong mineral acid and a little water be used, iodine is at once liberated.

With bromine in chloroform solution, the bromine is at once decolorised and hydrobromic acid evolved, and the residue on boiling with dilute alcohol gives bromoacetone. With ferric chloride, it gives a deep purple precipitate. It decolorises potassium permanganate at once in the cold.

With a mixture of silver nitrate and nitric acid, about 95 per cent. of the iodine is converted into silver iodide.

When dry and pure, light has very little action on it, but when moisture is present, it rapidly decomposes, giving acetic acid and other compounds.

## EXPERIMENTAL.

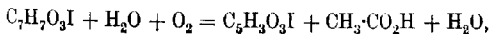
The best method for the preparation of the compound  $C_7H_7O_3I$  is the following:

Ten grams of dimethylpyrone are boiled with excess of barium hydroxide, the precipitated barium salt is dried and suspended in 150 c.c. of absolute alcohol, and 20 grams of iodine are carefully added with shaking. The barium salt gradually dissolves and then another barium salt begins to crystallise out. It is not necessary to separate this barium salt. About 500 c.c. of water are then added and some dilute hydrochloric acid. The compound  $C_7H_7O_3I$  at once separates. By making the mother-liquor alkaline with sodium hydroxide, evaporating off the alcohol, and acidifying again, a further small amount of the compound  $C_7H_7O_3I$  is precipitated. It is necessary to make the solution alkaline before evaporation because the compound  $C_7H_7O_3I$  is volatile with steam. From the residue a small amount of dimethylpyrone, and a compound that gives a deep purple colour with ferric chloride, can be extracted.

The pure compound  $C_7H_7O_3I$  can be obtained by crystallisation from dilute alcohol or from acetic acid. It seems to crystallise in two different forms, first separating as voluminous, needle-shaped crystals, that gradually change to small, granular crystals.

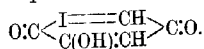
A number of analyses gave the following results: Mean, C = 31.5; H = 2.5; I = 47.1.  $C_7H_7O_3I$  requires C = 31.6; H = 2.6; I = 53.7 per cent. The yield of the compound is usually about half the weight of the dimethylpyrone employed. If all the dimethylpyrone were converted into  $C_7H_7O_3I$ , 10 grams should yield 21.4 grams; as a rule, only 5 grams are obtained.

When moist  $C_7H_7O_3I$  is exposed to sunlight, it decomposes rapidly, turning brown and liquefying, and acetic acid is formed in considerable quantities. The brown mass, when treated with absolute alcohol, leaves an orange-red precipitate. This substance can be dissolved in hot acetic acid and is precipitated in small crystals by the addition of water. When heated, it turns brown and decomposes violently at 185—190° with liberation of much iodine. It is acid to litmus, is easily soluble in sodium hydroxide solution, and does not contain water of crystallisation. Unfortunately, only small quantities of it could be obtained, and only an iodine estimation was made (Found: I = 54.0.  $C_5H_3O_3I$  requires I = 53.4 per cent.). It may have been formed according to the equation





when it would have the quinonoid formula



The *barium compound* that separates when iodine is added to the barium salt of diacetylacetone, crystallises in needles. It is insoluble in water, and when treated with dilute acids gives the compound  $\text{C}_7\text{H}_7\text{O}_3\text{I}$ . On heating, it decomposes, giving iodine. It contains water of crystallisation [Found, for material dried in a desiccator, Ba = 19.5; I = 36.4;  $\text{H}_2\text{O}$  = 5.5.  $(\text{C}_7\text{H}_6\text{O}_3\text{I})_2\text{Ba} \cdot 2\text{H}_2\text{O}$  requires Ba = 19.5; I = 36.1;  $\text{H}_2\text{O}$  = 5.1 per cent. Found, for material dried at  $140^\circ$ , Ba = 20.7.  $(\text{C}_7\text{H}_6\text{O}_3\text{I})_2\text{Ba}$  requires Ba = 20.5 per cent.].

*Acetyl Derivative.*—By heating the compound  $\text{C}_7\text{H}_7\text{O}_3\text{I}$  with acetic anhydride and a few drops of concentrated sulphuric acid, and then adding water, a semi-crystalline precipitate is obtained. This can be purified by dissolving in alcohol, decolorising with animal charcoal, and recrystallising. It forms white, granular crystals, m. p.  $68.5^\circ$ . It gives no colour with ferric chloride, and is acid to litmus paper. It can be distilled without decomposition. On keeping, it turns bright lemon-yellow, finally becoming orange. The mean of several analyses gave C = 34.6; H = 3.0; I = 41.1.  $\text{C}_7\text{H}_6\text{O}_3\text{I}(\text{CO} \cdot \text{CH}_3)$  requires C = 35.1; H = 2.9; I = 41.2 per cent. When the acetyl derivative is warmed with sodium hydroxide solution and the product acidified, the compound  $\text{C}_7\text{H}_7\text{O}_3\text{I}$  is precipitated.

*Phenylhydrazine Derivative.*—The compound  $\text{C}_7\text{H}_7\text{O}_3\text{I}$  reacts violently with phenylhydrazine, and water is given off. If, however, it is dissolved in a little alcohol and phenylhydrazine added, the mixture becomes warm, and a crystalline compound separates. It can be recrystallised from acetic acid. On heating, it rapidly turns brown and suddenly decomposes. It contains water of crystallisation, but decomposes below  $100^\circ$  [Found: N = 11.3; I = 25.0.  $\text{C}_7\text{H}_7\text{OI}(\text{N}_2\text{H} \cdot \text{C}_6\text{H}_5)_2 \cdot 3\text{H}_2\text{O}$  requires N = 11.2; I = 25.4 per cent.].

*Salts of the Compound  $\text{C}_7\text{H}_7\text{O}_3\text{I}$ .*—The compound was treated with excess of barium hydroxide, the excess being removed with carbon dioxide. The filtered solution was evaporated to a small bulk and alcohol added. The salt separated in long, white needles. These, when dried in a vacuum over sulphuric acid, turned lemon-yellow. The mean of several analyses gave Ba = 19.7; I = 35.8.  $(\text{C}_7\text{H}_6\text{O}_4\text{I})_2\text{Ba}$  requires Ba = 19.5; I = 36.1 per cent.

The *silver salt* is insoluble in cold water and slightly soluble in hot water. The *lead salt* has similar solubilities.

UNIVERSITY COLLEGE,  
GOWER STREET, LONDON.

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*Photosynthetic Processes in the Air, upon the Land,  
and in the Sea in Relation to the Origin and  
Continuance of Life on the Earth.*

HUGO MÜLLER LECTURE, DELIVERED BEFORE THE CHEMICAL  
SOCIETY ON JUNE 16TH, 1921.

By BENJAMIN MOORE, D.Sc., F.R.S.

MR. PRESIDENT, LADIES and GENTLEMEN,—In the course of this lecture I am about to attempt to summarise ten years' work. I should like at the outset to express my gratitude to several collaborators who have aided me on the subject—especially to my friend Mr. Edward Whitley, of Oxford, and to Mr. Arthur Webster, of London, who have assisted me throughout these researches.

The results obtained may be of practical interest to the botanist and to the chemist, and even to the economist; but it is not from any of those practical aspects that I would like to present the subject to you this evening, but rather from a philosophical point of view. The outset of the whole matter is:—How did living things come to be on this earth or on any other earth? It is a curious thing that I am standing up here talking to you this evening and that you are all listening to me, if you will reflect upon it that some millions of years ago this earth was a molten mass. Many theories have been put forward to explain how life did come to the earth, and how it could come to the earth. Some only pass on the problem to another world, and say that a germ was born in that distant world—that, either by radioactivity or by sunlight, or in some other way, this germ landed upon our earth, and so, by a fortuitous combination of circumstances, we are all here. There is not any modern theory which passes that limit. All the earlier theories as to how life arose seem to be lacking in that they do not start at the beginning of things. That is not to be wondered at. In the days of van Helmont, the Abbé Spallanzani, and those who succeeded them, and even in the days of Pasteur, people were looking for a sudden evolution of life. That is not a philosophical point of view. Life is not distinct from the inorganic. Any germ coming from another planet must have had the property of building energy, or it could not have existed. Therefore there must be some stages that lie between anything, even so simple as a single unicellular alga, and the inorganic world. There must be some possibility of tracing out a continuity right through from the inorganic to the organic and up to man.

It is a remarkable fact that evolution was first discovered in the organic world. It might at the outset seem probable that the chemist would be the first to discover evolution, but he was not. It was the biologist who discovered evolution, and the chemist is following in his footsteps.

It appears to me that the fundamental law in all evolution is the law of what might be called "complexity,"—that as soon as it becomes possible for matter to become more complex under the energy field in which it exists it obeys the law and becomes more complex.

In the sun, for example, even binary compounds probably do not exist at all. From all that astronomy and spectroscopy teach us, even such a stable element as iron is broken up into proto-elements. But as the inorganic environment changes it becomes possible for elements, as we know them on earth, to exist, and, at a later stage, it becomes possible for simple binary compounds also to exist. Always Nature proceeds on this law of complexity to a point at which, as will now be shown, it becomes necessary to establish a new unit.

I am not going to attempt to enter into the construction of the atom. I do not know enough to do so. But it seems that the electron is about the simplest thing possible. The electron, with some central basis and with a number of other electrons variously arranged, forms the atoms. The atom goes on evolving in complexity, and as it gets heavier and heavier and more complex there comes a period at which that unit reaches its maximum and as it reaches its maximum the element becomes unstable. It is just here that there appear the radioactive elements. But Nature is not to be baffled by this new situation. She proceeds to the simple inorganic compound, and she makes mono-molecules of the simplest type. Then she goes on and on with these until a new limit is reached. She adds on to the mono-molecules subsidiary molecules, such as the water of crystallisation, and, finally, a stage is reached at which fresh building up is impossible. It is not always reached at the same place, but a point in the average is reached where she cannot build up more complex molecules, and she then begins to build up colloids. She takes even quite simple molecules like silica ( $\text{SiO}_2$ ) and combines these into groups of fifty or sixty molecules. These acquire different properties as they go on. They become what Graham called metastable. Their reactions are much slower than those of the simple inorganic compounds, and so we pass on towards life. Always Nature is phasic, and the periodicity of movement becomes slower as the organism becomes larger and larger; and it is as it reaches these larger stages that it begins to react with outside forms of energy in a new manner.

It is curious that at the lower temperatures of the air radiant energy can come from the sun and build itself up again and form things like coal and petrol and all those combustible things from which one can make high explosives.

As the colloid becomes more complex it acquires the power to react to the light, and it is only when a stage has been reached at which reaction to light can occur that it becomes feasible to build up living creatures. If you reflect about it, it is really strange how biochemical energy, the energy of life, comes into everything. I do not believe there is a single object in this room that has not had biochemical energy concerned in the formation of it. Let us take this glass. How could that bottle have been made if there were not the energy of biochemistry to fasten the silicates into it? Ourselves, our clothes, the table in front of me, paper, everything practically that man is concerned with, arose from light. Light was at the beginning of all things living: there is no question about that. And it was in the water that they began. Three-fourths of our own bodies consist of water now. Nothing happens within our bodies that does not happen in solution. It was in the sea and the lakes that life first originated by the bearing down of the sun's energy upon these inorganic colloidal complexities which were beginning to form there.

Then there was adsorption as in the diatom. These inorganic colloids not only form the organic matter, but they build it up into their own cells; they form skeletons for it. And so we can trace, as we commence at these beginnings, how life began. We shall never trace it by studying bacteria. Bacteria could not exist in this new world. There is nothing for them to live on. There is no food for them. The condition is a thousand times worse than a famine strike; there is nothing to eat even. Nothing living could survive under such conditions that did not possess the property of building up the energy of the sunlight as it came down to it. It is an interesting discovery that in those early days it was the ultraviolet and the blue light that were used, just as a photographic plate uses these rays to-day, and as evolution has proceeded there have appeared more and more delicate sorts of transformers which must even be carefully protected from such rays and utilise instead the slower waves of the spectrum. As you all know, sunlight is germicidal to bacteria; they cannot be exposed to it, and so various colour screens have to be fabricated, such as chlorophyll, and many others, which protect this dawning life from being killed by the very sunlight which first originated it. Also it does not seem to have been the purpose of Nature, or whatever governs Nature, merely to evolve life, because several other changes,

which will now be considered, had to occur before life became possible down below.

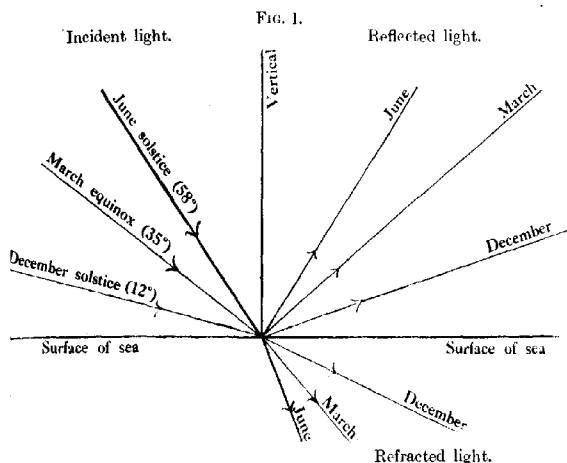
Let us think of the thing at the beginning. As the light from the sun first strikes the earth's atmosphere, perhaps one or two hundred miles above, it is full of ultra-violet light, and violet light. Such light rays as these, if they reached the earth at the present moment, would annihilate us; they would simply mean death to the world below.

The first thing that happens to prevent this is that ozone is developed, and by absorption this ultra-violet light is shut out. The solar spectrum of sunlight was known to the physicists to be marked out, to be limited, by the ozone developed in the upper atmosphere, and it has been shown that if there were only a millimetre of ozone interposed between quartz plates nearly all this light, which is germicidal light, would be shut out. It is not completely shut out as the light passes through the air and that is why there must be these natural colour screens in plants and animals and man. Bacteria cannot live in the open in the sunlight, and, as Marshall Ward showed, those fungi that live in the open and are not under the protection of green trees have to possess some colour developed within them, some pigment, so that this light is shut out.

Another interesting field and one that wants investigation is the effect of short wave-lengths of light on various gaseous mixtures. For example, nitrogen and oxygen unite under the influence of light, it is true only to a small extent, but they do combine and form nitrogen pentoxide and nitrogen trioxide. Also from nitrogen and hydrogen ammonia can be produced. All these changes are of great importance in the atmosphere, before the earth or the sea is approached.

Next, let us consider the sea, where life first started, and where, in the vegetable world, it has only in a comparatively small number of species got beyond the algal region yet. The reason why algae still form the preponderating bulk of marine plant life probably is that the external medium (sea water) gives perfect nourishment to the alga; it was when plants passed to new environment that further evolution was required to conserve the store of alkali. This conservation of alkali evolved in fresh water as a preliminary to terrestrial life. It is light then that produces the change in the springtime, and not temperature. At the end of this lecture I will show you a slide to demonstrate that clearly. When the temperature is at its lowest in the sea a tide of life suddenly bursts forth. As the spring advances the sun is getting higher every day, and the day is getting longer, and one can easily perceive that what might be called a critical angle is reached. I will draw what I mean on

the blackboard. Take this line to represent the surface of the sea, his arrow the light, and on a November or December day the sunlight is coming upon the sea surface. Not only is the day short and the light feeble, but practically none of the light will pass through. Now come to the equinox about March. Then the light breaks through into the sea, and just at that period there is a wonderful outburst of life before the temperature has risen at all. That is a most remarkable and interesting thing, and also a fact of practical importance, because, until that light comes to the sea,



This sketch illustrates the direction and intensity of light entering the sea at various seasons of the year at a latitude of  $55^{\circ}$  North. The sun's declination in June solstice being  $23\frac{1}{2}^{\circ}$  the altitude at noon is  $(90 - 55) + 23\frac{1}{2} = 58\frac{1}{2}^{\circ}$ , at the equinox in March the altitude is  $90 - 55 = 35^{\circ}$ , and in the December solstice it is  $35 - 23\frac{1}{2} = 12\frac{1}{2}^{\circ}$  only. The variation in the length of the day is also to be remembered. The optimum daily exposure is that of the spring; winter is too dark and summer too bright.

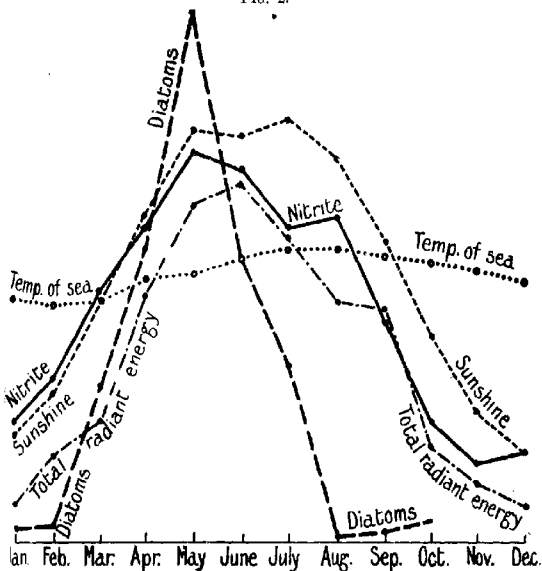
producing the minute floating green plants, the life of the crustacean leading up to the life of the herring and the food fishes cannot appear. This action of light is the beginning of the whole Spring in the sea. At a certain time the light penetrates into the sea water, and a day or two later the great sea breaks out into life, and there is a long concatenation of generations after that which lead up to the varied life of the sea. The amount of alkali developed as that light enters the sea and acts upon the floating algae suffices to turn the sea water alkaline to the most delicate indicator. Calcium bicarbonate and magnesium bicarbonate are taken out of the water,

discovery which really has been rejoicing me ever since. I have told you that if you expose marine algae to light, the solution in which they are exposed turns alkaline, because they build up the carbon dioxide and turn out the alkaline carbonates. After we had discovered that fact, I asked Whitley to continue the investigation at Oxford. He drew a complete negative. He could not get any alkalinity as evidence of photosynthesis in any of the fresh-water plants then used. We really could not understand the matter a bit—why we should get it in the sea and not get it in the fresh-water. Having been disappointed at Geneva, we turned round to try a whole series of these fresh-water plants from Lac Lemman to discover whether they would go alkaline or not, and what we found out as the result was that the fresh-water alga behaves like the marine alga, but that the higher fresh-water plant does not. It photosynthesises. It builds up nitrogen, but it does not give any alkali out to the surrounding medium in which it is growing. That is quite an interesting fact in itself, but if you think a little longer about it the interest increases, because it was only when that sort of semipermeable membrane for alkali established itself that it was possible for anything to emerge from the water and step ashore on to dry land. Any of the terrestrial plants, a tree or an herb or a blade of grass, cannot part with alkali. It cannot behave like a marine alga in the sea and take in bicarbonate and give out carbonate again. It must depend on what it takes up from its rootlets. It must have a supply of alkali in its own substance, and as the sunlight plays upon it it must take in *free* carbon dioxide from the atmosphere, and keep on all the time, using over and over again that same supply of alkali that it possesses. In other words, it must possess a regulation of alkalinity. It is the rudimentary trace of that preservation of alkalinity which runs right up to man from this point at the beginning of organised beings.

In order that animals can flourish on the land, and in order that the whole terrestrial civilisation can arise, there must develop a system by which the land plant takes its alkali up from the root, retains this store of alkali, and simply takes in free carbon dioxide and utilises its alkali over and over again to form bicarbonate on which the sunlight plays and produces organic matter. The point—and rather a beautiful point—is that all this evolution happened in the fresh water before the plants emerged. Above the algal level that new order of things does establish itself, and the higher aquatic plant in fresh-water resorts to terrestrial habits, and establishes this condition of affairs, then it can emerge and all terrestrial life commences. It is one of the earliest of these adjustments. Of course, physiologists know other fundamental adjust-

agents at different levels. For example, at a certain stage in the evolution of fishes there was such an adjustment of the salt level. The great majority of the fish that are in the sea, including all edible fish, are not any saltier than fresh-water fish. They develop what is called a certain "tonicity" in their blood, and that saline adjustment, once it has been established, persists right up to man through all the intervening species. In the same way, we get an adjustment of respiration. You can kill a mammal if you over-breathe it. In my opinion, a great deal of the evil effects of what

FIG. 2.



was called "shock" during the war, and is called "shock" still by the surgeon, is due to a variation in the adjustment of that degree of alkalinity. Here then, right down at the algal level, we find now the very first traces of the adjustment of the reaction, and of a condition of affairs which makes it possible for life to emerge on the land.

Now I will turn to some of my lantern slides, and show you the figures in support of what I have been saying.

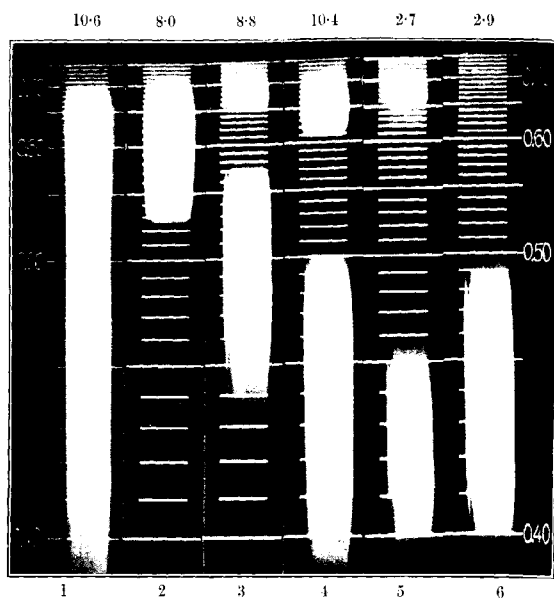
Figure 2.—Here there is represented a compilation of a series of different data. I cannot claim credit that any line of the series



of data belongs to myself. All I can claim is that I correlated them. On the base-line you see marked out the months of the year. Then there are several curves above the base-line which are plotted to different scales. They are so plotted as to bring them together so that you can study them. The units used in plotting do not particularly matter and need not now be described. The point is not exactly how the curves rise, but the interest rather lies in how they follow one another. You will see there is one curve that does not follow the others, and that is the temperature of the sea at Port Erin, Isle of Man, over an average of ten years. We come next to the diatoms in the sea on which the life of the fishes depends. Observe that in February there are very few diatoms. The light, remember, is increasing all the time, and between February and March you see how they increase and get to their maximum about April. Then the light gets too strong for them and they come down again, and in the winter months after August they come quite low down. Look next at the sunshine curve following so closely the numbers of diatoms. Another curve shown there is the total radiant energy. The curve showing "nitrite" is the average amount for the last fifty years at Radcliffe Observatory, Oxford, of what used to be called "ozone." There is not any ozone on the surface of the earth. The substance present and formerly taken for ozone is nitrogen trioxide, and it is quite interesting to speculate as to what that means in the air at the surface of the earth. It was supposed that the nitrites and nitrates in the air were derived from thunderstorms. There is not the least evidence at all to support this view. You can take the rain that falls after a thunderstorm and you will find no more nitrite in it than you will find in an ordinary shower. The amount present at any given time does not follow the amount of electric disturbances in the air, and you can see by the diagram, on the other hand, how very closely it does follow the sunshine. That is quite an interesting point, because plants take up these nitrites from the air and nourish themselves from it, and there is a considerable amount of direct nutrition of plants accomplished in that way by the simple taking up of nitrites. I think also it is worth the while of the chemist to look into the matter from the point of view as to how accumulations of nitrites occur on the earth's surface. Such deposits are usually found in Peru and India, where there is so little rain to begin with, where there is intense sunlight, and where there probably is some supply of alkali to fix the nitrogen trioxide, because we do not find it as acid, but as the salts, sodium nitrate and sodium nitrite. Another important photosynthetic reaction is that by which nitrates pass over into nitrites. To carry it out you want



FIG. 3.



This series of spectrograms, and the figures for alkalinity developed as shown over each spectrum, illustrate the photo-synthetic activity of each part of the solar spectrum, and demonstrate that all regions are utilisable and not merely the regions of the absorption bands of chlorophyll. It is also to be noted, as described in the text, that the longer wave-lengths in red, yellow, and green are the most active. From left to right the coloured screens are to the eye: No. 1, full spectrum; No. 2, red screen; No. 3, green screen; No. 4, yellow screen; Nos. 5 and 6, blue and violet screens.

My thanks are due to Mr. J. E. Barnard, late President of the Royal Microscopical Society, for taking these spectrograms for me.

nothing more elaborate than an ordinary soup plate, putting into it a solution of one part in ten thousand of sodium nitrate, exposing it for an hour or two to such sunshine as we are having at present, and you will get an intense reaction, showing that nitrite is developed. That reaction means the uptake of energy. The number of these endothermic reactions that we have hitherto discovered is very small. The one in the green cell is the most predominant of all, but a similar reaction occurs between nitrates and nitrites with uptake of the energy of the light. That is without a green cell at all. In the presence of a green cell you get a fixation in the form of protein of amino-nitrogen from the atmosphere when you have no nitrate whatever present. That has been disputed for about one hundred and fifty years, but after a good deal of work I have not the remotest doubt that both the lower and higher plants do build up nitrites and nitrates and form organic nitrogenous compounds from the free nitrogen of the atmosphere. Those are the main points about that diagram. What I want to point out is that the outburst of Spring has not much to do with the temperature of the sea, but it has a great deal to do with the amount of sunshine. A great deal of our life, unconsciously to us, is bounded by sunshine. Many unhealthy lives are produced by the lack of sunshine. If you get either too much or too little sunshine, there is ill-health over the whole world. We do not realise at all to what extent we are dependent on a properly modulated amount of sunshine throughout the year.

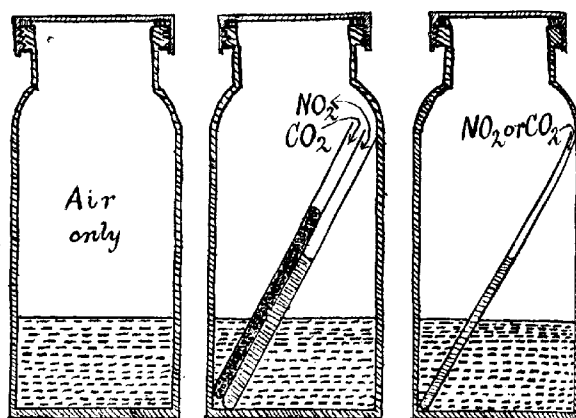
Figure 3.—This is an experiment showing to what extent different regions of the spectrum take a part in photosynthesis. You see the spectrum under a plain glass under sunlight only showing 10.6 c.c. of alkalinity\* after a given exposure. Then we get 8 c.c. with that simple bit of reddish-yellow light shown in the second spectrum alone remaining for photosynthetic action. In the fourth one there is almost as much, namely, 10.4 c.c., as in the full sunshine, although all the intermediate parts of the spectrum are shut out. The next two show how poor the blue light is in producing photosynthesis, the amounts being 2.7 and 2.9; this is, of course, quite different from the photographic plate. There are two things shown by this set of spectra and their accompanying figures. First of all, that it is not merely in the region of the absorption bands of chlorophyll that photosynthesis occurs, but all throughout the spectrum. And secondly, that there has been evolved in the living green cell a mechanism, contrary to those

\* That is, when 10 c.c. of sea-water in which the alga has grown are titrated with N/100-sodium hydroxide. The time of exposure was about five hours in all cases.

utilised in the beginning of organic things and to those affecting our photographic plates and ordinary chemical processes, a mechanism dealing with lower wave-lengths, and one which has to protect itself, by its colour screen, from the blue and ultra-violet, or else it gets killed.

Figure 4.—This experiment shows how growth may be stimulated by adding artificially oxides of nitrogen or sodium bicarbonate. What I did was to take a closed jar with a screw-down top and then in some cases put slanting side-tubes in, leaning

FIG. 4.



To illustrate arrangement of screwed-down jars to show fixation of nitrogen and carbon. Similar arrangements can be made to demonstrate the nutrition of algae from methyl alcohol, formaldehyde, and other poisonous simple organic substances. The nutrition tubes must be so narrow that the algal cells can utilise the poisonous nutrients as rapidly as they are evolved.

against the wall of the jar. In some cases no tubes were inserted and in others simply a little solid sodium bicarbonate, in others a system which would slowly evolve nitrogen trioxide and in still others tubes which could evolve both gases. You see the amount of fixation of nitrogen in each case. With no additions at all, with the vessel quite closed up, one gets almost 4 milligrams of fixation of nitrogen. A small figure, you may say, but it is no smaller than that on which previous observers depend for all proof of the nitrogen-fixing bacteria and azotobacter. Then, if you put in some sodium bicarbonate you get an increase in the figure from 3.46 to 5.1; that is to say, the small partial pressure of carbon

dioxide coming back from the sodium bicarbonate took the place of the carbon dioxide of the air which got exhausted in the jar when it was closed, and if you supply the sodium bicarbonate so that you get carbon dioxide coming out of the side tube, then at once this increase in fixation of carbon commences. I simply put a very narrow piece of glass tube drawn out like a test-tube into the sealed jar, with either one tube of sodium bicarbonate, or two tubes, one containing sodium bicarbonate and the other a little nitrite and very dilute acid to give off a small amount of nitrogen peroxide. You see the effect when you supply both. That is what manures do. They provide that stimulus at a certain period when the young plant wants it, to produce more rapid and enforced growth. They are stimulants similar to what physiologists call accessory food-stuffs. They carry the plant on through a certain stage, and I think that is the main purpose of manures and not direct building into the plant. The weight of rich manures supplied is many times smaller than the increase in the crop. Manures remove certain limiting factors of growth.

	Nitrogen fixed.
Nos. 1 and 2 (no additions) .....	3.46 mg.
Nos. 3 and 4 (sodium bicarbonate only) .....	5.40 "
Nos. 5 and 6 (oxides of nitrogen only) .....	2.50 "
Nos. 7 and 8 (both sodium bicarbonate and oxides of nitrogen) .....	14.10 "

#### ENDOTHERMIC FORMATION OF NITRITES FROM NITRATES.

The amounts of heat involved and differences in transition from one oxide of nitrogen to another are shown in the following table given by Mendeléeff, in which the numbers in the upper row represent thousands of gram-calories for a gram-molecular formation from the elements; and the lower shows in thousands gram-calories the heats of transition from one oxide to the other:

$\text{N}_2\text{O}$	$\text{N}_2\text{O}_2$	$\text{N}_2\text{O}_3$	$\text{N}_2\text{O}_4$	$\text{N}_2\text{O}_5$
-21	-43	-22	-5	-1
	-22	+21	+17	+4
		→		

This table shows that in passage from  $\text{N}_2\text{O}_5$  to  $\text{N}_2\text{O}_3$ , a supply of energy must be given to the reacting system amounting to  $4 + 21 = 25$  thousands of gram-calories for each gram-molecule converted.

This table shows that there is an endothermic effect or absorption of light energy in the building up of the nitrogen trioxide.

The top line shows the amount of energy. If you take nitrate—*this* extreme right side—and pass that into  $N_2O_3$ ; that is to say, from nitrate to nitrite—and the sun does that for you—there are 21 kilo-calories per gram-molecular weight going from  $HNO_3$  to  $HNO_2$ . This is a very considerable accumulation of energy and it is going on all the time wherever nitrates are exposed to sunlight. We have known for a very long time the same thing about carbon. We have only recently acquired the same knowledge about nitrogen. If you get the inactive nitrates coming up from the soil into the leaf and being exposed to the sun, that action proceeds with the uptake of energy, and these nitrites are ever so much more active physiologically than are the nitrates, and that is the beginning, in my estimation, of the formation of the proteins in the plant—that you first of all get your nitrates to your nitrites. Ordinary running water as it comes down, or dew, contains these nitrites. If you allow water to stand for a day or two in the dark, or in a cistern or reservoir, or take it from an ordinary tap, you get no nitrite; but you have only to take that tap water, or water that has stood for some time, and put it in a soup plate in the face of the sun for two or three hours, and you get your reaction of nitrite at once. An endothermic reaction takes place and the nitrite is formed from a nitrate.

#### FIXATION OF NITROGEN BY MARINE ALGÆ.

##### CONDITIONS OF EXPOSURE TO LIGHT.

###### *Exposures.*

Nos. 1 and 2.—Kept with lids tightly screwed on in such daylight and sunlight as were available outdoors.

Nos. 3 and 4.—Ditto, but instead of tightly screwed-on lids, these were covered above only with a double layer of muslin, so that there was free access of atmosphere.

Nos. 5 and 6.—Exposed to diffuse light only indoors on shelf in laboratory, with lids tightly screwed on.

Nos. 7 and 8.—The same as to light, but open, with muslin covers only.

Nos. 9 and 10.—Kept in complete darkness in cupboard with lids tightly screwed on.

Nos. 11 and 12.—Also kept in darkness in cupboard with muslin covers only.

*Results.**Experiment of March 28th—April 5th, 1919 (seven days' interval).*

1.	2.	3.	4.	5.
Nature of exposure.	Daily titration in c.c. of $N/100$ -acid in 100 c.c. of the culture required to neutralise to phenolphthalein on the dates given.	Wet weight at end. Initial weight in each case, 2 grams in 800 water.	Dry weight at end. Grams.	Total nitrogen by Kjeldahl. In mg. for entire period.
	April 2.	April 5.		
1. Sunlight, in <i>shut</i> jars, out-doors .....	13.3	9.7	2.57	0.476
2. Sunlight, in <i>open</i> jars, out-doors .....	6.7	9.7	2.38	0.457
3. Diffuse light, no direct sun, on shelf indoors. Shut jar.....	0.4	3.4	1.71	0.284
4. Same exposure as No. 3, but jars open .....	0.0	+1.7	1.47	0.285
5. Darkness, in cupboard. Shut jars .....	-1.7	-1.4	1.45	0.259
6. Same as 5, but jar open .....	-1.2	-0.3	1.50	0.275

NOTE.—At the end the contents of each pair of similarly exposed jars were united for purposes of analysis so that No. 1 in "Results" corresponds to Nos. 1 and 2 in "Exposures," No. 2 in "Results" to Nos. 3 and 4 in "Exposures," and so on.

These results show the fixation of nitrogen by marine algæ. Nos. 1 and 2 were exposed to sunlight. No. 1 was in a closed jar, and No. 2 was in an open jar. Nos. 3 and 4 were in a diffused light. Nos. 5 and 6 were kept in darkness. The jars in light were exposed for five days with fair sunshine, not nearly so intense as we are enjoying at present. You see how the wet weights run up and down in light or dark. They were all 2 grams to start with, and you see how the ones in the sunlight have gone up, and the others down, although the jars were shut in several cases. Next there is the dry weight, which shows a similar condition of affairs, and then there is the total nitrogen estimated by the Kjeldahl method. Fixation of nitrogen takes place without any appearance whatever of the production of bacteria. They remained perfectly clear, and to fix that amount of nitrogen by the azotobacter the amount of turbidity would be unmistakable. All observers on such bacteria state that their media became turbid or milky. These algal growths do not get milky. I do not want to pursue that argument too far, but it seems to me that it is intensely interesting—whether it is done by two things working together, one of which is a bacterium, or by the green cell alone. Suppose we grant there are bacteria. There is an association of



the two things together. There is a process instituted by which an energy transformer can take hold of sunlight, and by means of that sunlight capture the nitrogen of the atmosphere and convert it into proteins. That is far more important than worrying ourselves as to whether it is done by the green plant alone, or by the green plant plus some bacterial agency.

The table given below shows in similar fashion the fixation of nitrogen by fresh-water algæ. The organisms were simply sewn into each jar in fresh-water.

In order to save space in tabulation the amounts of nitrogen found by the Kjeldahl determination carried out at the conclusion of the experiments are here placed opposite the description of the treatment of each jar:

No. 1.—Tap-water and algæ only, glass lid screwed down, kept in light. N = 0.3 mg.

No. 2.—Tap-water and algæ only, no glass lid, top covered by fine lawn, kept in light. N = 1.6 mg.

No. 3.—Tap-water and algæ only, screwed down, no glass lid, kept in darkness. N = 0.1 mg.

No. 4.—Tap-water and algæ only, covered by fine lawn, kept in darkness. N = 0.3 mg.

No. 5.—Tap-water, algæ, 2 c.c. of 5 per cent.  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  (that is, 0.05 per cent. of  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ ), lawn cover only, kept in light. N = 8.1 mg.

No. 6.—Tap-water, algæ, 0.05 per cent. of  $\text{Na}_2\text{HPO}_4$ , screwed down glass lid, kept in light. N = 1.0 mg.

No. 7.—Tap-water, algæ, 0.05 per cent. of  $\text{Na}_2\text{HPO}_4$ , 0.05 per cent. of  $\text{NaNO}_2$ , lawn cover only, kept in light. N = 12.3 mg.

No. 8.—Tap-water, algæ, 0.05 per cent. of  $\text{Na}_2\text{HPO}_4$ , 0.05 per cent. of  $\text{NaNO}_2$ , screwed down glass lid, kept in light. N = 0.7 mg.

No. 9.—Tap-water, algæ, 0.05 per cent. of  $\text{Na}_2\text{HPO}_4$ , 0.05 per cent. of  $\text{NaNO}_2$ , formaldehyde vapour at high dilution supplied from side-tube as described below, glass lid screwed down, kept in light. N = 3.8 mg.

No. 10.—Tap-water, algæ, 0.05 per cent. of  $\text{Na}_2\text{HPO}_4$ , no  $\text{NaNO}_2$ , formaldehyde vapour, glass lid screwed down, kept in light. N = 1.0 mg.

No. 11.—Tap-water, algæ, 0.05 per cent. of  $\text{Na}_2\text{HPO}_4$ , 0.05 per cent. of  $\text{NaNO}_2$ , dilute methyl alcohol vapour supplied from side-tube, glass lid screwed down, kept in light. N = 7.4 mg.

No. 12.—Tap-water, algæ, 0.05 per cent. of  $\text{Na}_2\text{HPO}_4$ , no  $\text{NaNO}_2$ , dilute methyl alcohol vapour from side-tube, glass lid screwed down, kept in light. N = 1.1 mg.

It is observable from the particulars given for assimilated nitrogen

that this occurs even when no nitrogen is supplied. Any nitrogen supplied from without is returned and more with it, but even in those cases where none is supplied to the plants they still grow and fix organic carbon and nitrogen. Another quite interesting point shown in that experiment is that you can use things which are very poisonous to plants to supply them with food, if only you conduct the thing in the proper way. There has been a long-continued dispute over von Beyer's hypothesis that formaldehyde is the first substance formed in the photosynthesis in the way of carbon compounds, and observers have put formaldehyde, in various concentrations, into solutions, and usually they found that it killed the plant cells. On the other hand, if you take extracts of chlorophyll from plant tissues and expose them to the light they form formaldehyde themselves. These processes are reversible. The way to get at the thing with some success is not to put the formaldehyde or these other poisonous things into the solution, but to use a side-tube such as has been sketched above (Fig. 4, p. 1566). You just put your ordinary medium down with the materials in it, and place in the side tube formaldehyde in a dilute condition. Then you get the effects observed in the table given above, Nos. 9, 10, 11, 12. The nitrogen gets fixed. The formaldehyde is built into carbohydrates, fats, proteins, and other materials. This occurs only with a certain intensity of light. The germicidal action of sunlight may simply be a reversal of that process. If you take a green cell and expose it to ultra-violet light, you have to expose for a very long time before it is injured. If you take a thing like a tubercle bacillus—in fact, any colourless bacteria—and expose it, you will kill it in a minute or two. The poison may not be formaldehyde alone, for it is remarkable how organic compounds and living organisms disintegrate under the action of light, forming simpler and lethal substances. If you can imagine the living cell being invaded by formaldehyde produced by the action of light, you can readily see how it can be killed. All things in Nature are reversible. The world does not always go in the same direction. One time it is building up, and another time breaking down, just like the coming of the Summer and the Winter, and all the cycles that occur in Nature. Take such things as the heart-beat. It contracts; that is its period of activity. It relaxes; it carries out exactly the reverse process. Everything in Nature is phasic, and it is as a result of that phasic variation that we are able to progress in evolution and build up from one thing to another. Take all the pools round the coast. In winter they are acid. As the spring goes on they get more and more alkaline. You see the possibility that is expressed there for producing natural variations. One pool

may be considerably more alkaline than another, and some new birth of creature may arise in it simply because its reaction is entirely changed. It is only due to the conservative processes of Nature that we do not get a series of weird races and things arising to every change of environment. Nature millions of years ago invented methods by which the reactions of our bodies, the fluids of our own bodies, are kept within excessively narrow limits, and it is probable to my mind that it may be variations outside those limits occurring in these ways which cause new species of creatures to arise. There is all the time a stability. I want to impress that as the key-note of the whole thing. The pot seems to boil over, so that from a position of extreme instability it passes once more over into a position where it is stable and can begin to make a new movement forward. It goes up from the electron right into our social relations of the present time. We all know how the pot is boiling now. We do not know what is going to happen to the pot, but even at the level of sociology there is this same principle going right through that starts out at the beginning. Evolution has its periods of activity and its periods of rest, and I am quite certain that it was nothing fortuitous whatever that brought life to this world, and that given the same train of chemical and physical events in any other part of the universe, I will not say that human beings may have arisen, but the same changes and complexities must absolutely have arisen. There must be thousands of worlds in which there is some form of life, some form of activity comparable to our life, and intrinsically in its essence the same as our life.

#### BIBLIOGRAPHY.

Part of this lecture relates to matters which have not been published before, such as the sudden outburst of Spring on land and sea, and the transparency of the screen overlying chlorophyll under the twigs before the new leaves appear. The remainder has chiefly been recorded in the *Proceedings* of the Royal Society during the past ten years. The whole has been drawn together in a volume recently published by Mr. Edward Arnold entitled "Biochemistry, a Study of the Origin, Reactions, and Equilibria of Living Matter." An earlier account will be found in a volume in the Home University Library on "The Origin and Nature of Life."

CLXXXIII.—*The ortho-Dimethylantraquinones and their Derivatives.*

By ARTHUR FAIRBOURNE.

THE original reason put forward in favour of the accepted or 2 : 3 structure for the only previously known *o*-dimethylantraquinone, and for its derivatives, was based on analogy showing the improbability of formation of the 1 : 2-dimethyl isomeride during the dehydration of *o*-3 : 4-dimethylbenzoylbenzoic acid (Elbs and Eurich, *Ber.*, 1887, **20**, 1361; Elbs, *J. pr. Chem.*, 1890, [ii], **41**, 6), an argument still held to be valuable (Barnett, "Anthracene and Anthraquinone," 1921, 33). Before the war, however, the author, who was then working with Dr. Weizmann in Manchester University, succeeded in separating a product from this particular dehydration which was quite unlike the quinone described in the literature, but which gave evidence, nevertheless, of capability of bromination and of oxidation to an *o*-dicarboxylic acid.

It appeared probable, therefore, in spite of the arguments previously put forward against the likelihood of its being produced, that this was the unknown 1 : 2-dimethylantraquinone, or, alternatively, that it was the 2 : 3-dimethylquinone, and that the substance hitherto accepted as having the 2 : 3 structure was in reality either of a different constitution, in common with all substances derived from or connected with it, or was a mixture of the 1 : 2 and the 2 : 3 isomeric forms.

In the event of its being a mixture of this kind (compare variations of more than twenty degrees in the melting points of the specimens described by Elbs and Eurich and by various other experimenters; Limpricht, *Annalen*, 1900, **312**, 99; Willgerodt and Maffezzoli, *J. pr. Chem.*, 1910, [ii], **82**, 205; Heller, *Ber.*, 1910, **43**, 2890), then the additional evidence for the accepted 2 : 3 structure of all these substances which has arisen (Barnett) from the dissimilarity of the corresponding dicarboxylic acid, m. p. 340°, obtained by the oxidation of this dimethylquinone (Elbs and Eurich), with that obtained from other sources (Scholl and Swinger, *Ber.*, 1911, **44**, 2992), m. p. 268°, and undoubtedly having the 1 : 2 structure, is rendered uncertain, since the former acid of high m. p. obtained by Elbs may have come from either constituent of the isomeric mixture on oxidation, a possibility independently indicated by the fact that the latest worker (Heller) finds that this acid, made by the method of Elbs and Eurich, but obtained

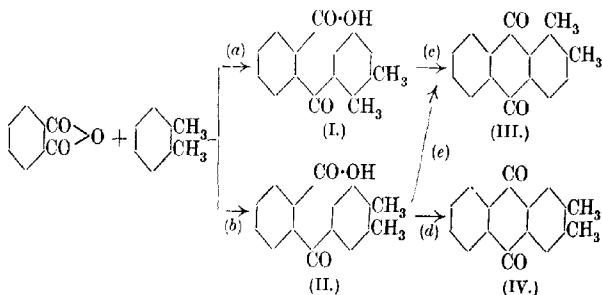
in a purer condition, does not melt at  $340^{\circ}$ , the temperature they state.

Moreover, the only remaining argument in favour of the 2:3 structure for all these substances (Elbs and Eurich) is that on reduction a dimethylantracene has been produced, whilst a substance with a methyl group in the position 1 would in all probability have given quite a different type of compound, owing to the simultaneous interaction of this methyl group with the reduced carbonyl group of the anthraquinone radicle; but this argument is also rendered invalid, since the specimen of dimethylantracene obtained may, like the dicarboxylic acid just mentioned, have come from either constituent of the isomeric mixture used, especially as no good yield is claimed in the description of this experiment.

For some time after the conclusion of the war *o*-xylene was unobtainable, and the author wishes to take this opportunity of expressing his thanks to Professor Crossley for very kindly offering a large private supply of this pure chemical to enable the work to be restarted, and the problem of the structure of these materials to be solved.

Phthalic anhydride and *o*-xylene were allowed to react in the presence of aluminium chloride to give *o*-dimethylbenzoylbenzoic acid as usual, and this acid was then dehydrated in a manner similar to that used by previous experimenters, but both possible *o*-dimethylantracenequinones resulted, and each has successfully been isolated.

At first, in view of the published statements already referred to, that reaction (e) was very improbable, it might be supposed that

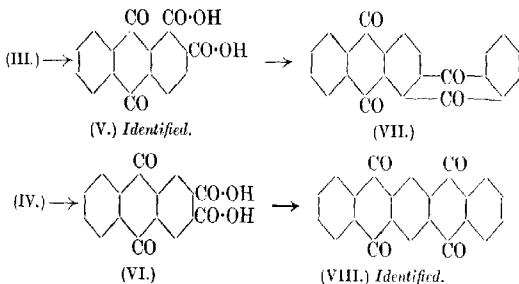


the isolation of both III and IV (although it was not known which product was represented by which formula) necessarily proved the existence both of I and II as requisite intermediate products in reactions (a and c) and (b and d) respectively; but subsequent careful fractional crystallisation of the sharply melting benzoyl-

benzoic acid used, and separate dehydrations of the successive crops of crystals obtained in this way from different solvents, have always yielded both quinones in quantity, whence the whole of the benzoylbenzoic acid used is proved to have the structure II, since I would be incapable of yielding IV by any reaction, a conclusion as to the structure of the acid which is in accordance with previous beliefs and proofs (Meyer, *Ber.*, 1882, **15**, 636).

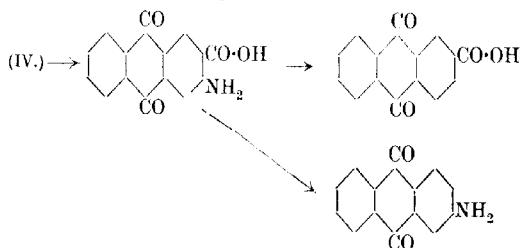
From this proved constitution of the specimens of acid actually used in these particular experiments, it necessarily follows that products III and IV must have the constitutions here assigned to them, unless wandering of the methyl groups has occurred; and such wandering, moreover, does not take place during these reactions, for, as will be shown later, each of these isomerides oxidises to a corresponding *o*-dicarboxylic acid capable of forming an anhydride.

The proof as to which isomeride is represented by the 1:2- and which by the 2:3-dimethyl structure has been achieved by comparing these acids with the 1:2-dicarboxylic acid prepared by Scholl and Schwinger; and has then been independently confirmed by condensing both the 1:2- and the 2:3-anhydrides with benzene to give 1:2-phthaloylanthraquinone (VII) and dinaphthantraquinone (VIII) (compare Philippi, *Monatsh.*, 1911, **32**, 631; Scholl and Seer, *Annalen*, 1912, **394**, 159; Mills and Mills, *T.*, 1912, **101**, 2194) respectively, thus:



As shown by the above formulae, the established identity of these products satisfactorily fixes the structure of all the materials involved, the quinone with m. p.  $150^\circ$  being therefore the 1:2-dimethylantraquinone, and the other, m. p.  $208^\circ$ , the 2:3-dimethylquinone. Elbs and Eurich, whose quinone melted at  $183^\circ$ , must consequently have been dealing with a mixture of these two, and the specimens of higher m. p. described by Limpriht, m. p.  $200^\circ$ , and Heller, m. p.  $205^\circ$ , must also have been

mixtures, but increasingly rich in the 2:3-dimethyl isomeride. Of these, only the specimen (m. p. 183°) of Elbs and Eurich was employed for supposed structural identification, and, as is now seen, it must certainly have contained the quinones of both possible *ortho*-structures in very considerable quantities, and it must, moreover, have given rise therefore to mixed derivatives belonging both to the 1:2 and the 2:3 series of substituted anthracene and anthraquinone products. Further, the quinone described by Willgerodt and Maffezzoli, and supposed by them to be the pure 2:3-dimethyl isomeride, which they used in their preparation of the dicarboxylic acid required for the attempted synthesis of the anthraquinone analogue of indigo, was almost certainly the same mixture as that used by Elbs and Eurich, since its preparation was stated to be identical with theirs, and since no difference was recorded between its properties and those which Elbs and Eurich had already described. This lack of evidence as to isomeric purity is doubly unfortunate in this particular case, in so far that not only are the constitutions of all the interesting substances synthesised thus rendered uncertain (for, from the details given, some at least, for example, the dicarboxylic acid and its anhydride, must have been mixtures), but, also, although it has never been so claimed, their work would have been an entirely successful determination of the structure of all these *ortho*-disubstituted anthraquinones now in doubt, had the isomeric purity of the initial dimethylquinone previously been assured; because from this dimethylquinone the dicarboxylic acid was prepared (m. p. not stated) and this was successfully converted into an anhydride, imide, half amide, and amino-acid, and the last compound was proved to have both its amino- and its carboxyl groups in  $\beta$ -positions by the elimination of each alternatively, leading to identifiable  $\beta$ -monosubstituted anthraquinones in both cases, thus:



A repetition of this work with either of the now separated isomerides has not, however, as yet been undertaken, owing to the previously mentioned method of determination of structure having

offered less experimental difficulty, and having afforded, in addition, an independent confirmation of the structure of the second isomeride, and of its 1 : 2 series of derivatives, as already explained.

Anthracene- and anthraquinone-2 : 3-dicarboxylic acids, 2 : 3-dimethylanthracene and dimethylanthranol, the above-mentioned compounds of Willgerodt and Maffezzoli, and all substances connected with these, are examples of compounds the characterisation of which has suffered from the existence of this unsuspected 1 : 2-dimethyl isomeride in what has previously been accepted as the pure 2 : 3-quinone. Certain of these compounds have now been prepared isomerically pure, as described in the experimental portions of this paper, whilst others, and also many corresponding reactions in the 1 : 2-series, are at present under investigation by another member of this College.

#### EXPERIMENTAL.

##### *o*-3 : 4-Dimethylbenzoylbenzoic Acid : Absence of its Isomeride.

This was prepared by reaction (a), the method of Elbs and Eurich (*loc. cit.*; compare Limpricht, *loc. cit.*; Willgerodt and Maffezzoli, *loc. cit.*; Heller, *loc. cit.*), but after the acid had been obtained in a pure condition with a sharp melting point, it was, nevertheless, fractionally crystallised from chloroform, and also from acetic acid, many times, the various crops of crystals being then separately submitted to reactions (c) and (d) as described below. Since both these possible dehydrations always occurred simultaneously, yielding both III and IV in quantity from every fraction of acid used, all confusion due to the possible presence of *o*-2 : 3-dimethylbenzoylbenzoic acid (I) in the following experiments has been entirely eliminated, this isomeride being incapable of yielding IV under any conditions; and thus the arguments used in the theoretical and in subsequent portions of this paper have been justified, and any trouble which might otherwise have arisen owing to the possible presence of the *m*- or *p*-isomeride in the *o*-xylene has also been obviated.

##### 1 : 2-Dimethylanthraquinone (III).

A mixture containing about 80 per cent. of the 2 : 3- and about 20 per cent. of the 1 : 2-isomeride was prepared by reactions (c) and (d) simultaneously from each of the fractions of the dimethylbenzoylbenzoic acid mentioned above, by a method similar to that used by Elbs and Eurich, and later investigators, for the preparation of the mixed quinones. One part of the benzoyl-



benzoic acid dissolved in 10 parts by weight of concentrated sulphuric acid was warmed gradually to 125° during half an hour, kept at this temperature for fifteen minutes, and then poured on ice. The precipitated light yellow powder was filtered, washed with water, sodium hydroxide solution, and again with water, and dried in a steam-oven. The dry powder, the yield of which was almost theoretical, was found to correspond with what previous experimenters have described as slightly impure 2:3-dimethyl-anthraquinone.

The 1:2-dimethylquinone was isolated from this mixture by taking advantage of the varying solubilities of the isomerides in acetic acid and acetone. A solution containing 12 c.c. of boiling glacial acetic acid for every gram of the isomeric mixture was filtered, allowed to cool, and kept during one hour. The crystals obtained were removed, and the mother-liquor was largely diluted with cold water, when a very pale powder separated. This was filtered off, washed with sodium hydroxide solution and water, dried, and crystallised from acetone several times. Quick crystallisation, caused by the addition of a small quantity of the pure material to the cooled, supersaturated solution, was used after this had once been obtained, and filtration was then carried out before crystallisation of the 2:3-isomeride had taken place. In some cases a final crystallisation from glacial acetic acid was also performed in order to leave the product in a state comparable with that of its isomeride in these experiments, but this had no effect on the properties of the washed and dried substance. From either solvent small clusters of nearly white needle crystals, m. p. 150°, were obtained, soluble in ether, alcohol, or benzene, and stable to alkalis and to hot alkaline potassium permanganate. A red coloration was produced, however, when this material was treated with ammonia and zinc dust (Found: C = 81.2; H = 5.1. Calc., C = 81.36; H = 5.08 per cent.). Its structure is proved by its method of formation and its oxidation to the 1:2-dicarboxylic acid described below, and is confirmed by the condensation of its 2:3-isomeride with benzene, as has been explained in the theoretical portion.

#### *2:3-Dimethylantraquinone (IV).*

The isomerically pure 2:3-dimethylquinone was obtained from the crystals deposited during the first, or acetic acid, crystallisation referred to in the preceding preparation. These were recrystallised several times from fresh glacial acetic acid, then washed with water, and dried in an air-oven. With the exception of the higher melting point (208°) already referred to, the properties of this

substance did not differ from those given by previous experimenters for the unseparated isomerides (Elbs and Eurich, *loc. cit.*; m. p. 183°) (Found: C = 81.3; H = 5.1. Calc., C = 81.36; H = 5.08 per cent.).

*Anthraquinone-2:3-dicarboxylic Acid and its Anhydride.*

The isomerically pure 2:3-dimethylantraquinone was oxidised to the corresponding dicarboxylic acid in a manner similar to that by which Elbs and Eurich oxidised the mixed quinones. One part by weight of the pure quinone was heated with seven parts of diluted nitric acid (D 1.1) at 200° for six hours. The crystalline product was filtered, washed with water, and recrystallised from acetic acid. The crude product, the yield of which was almost theoretical, did not melt at 350° (compare Elbs, m. p. 340°). In its general properties it was in agreement with Elbs' dicarboxylic acid; no coloration was produced during solution in alkalis, however, unlike the specimen described by Elbs, which appears therefore also to have been a mixture of the two possible isomeric forms, as were the quinones from which it was made. The acid readily passed into an anhydride by treatment with acetic anhydride, or by fusion or sublimation. This did not melt at 300° (compare Elbs and Eurich, m. p. 290°), but otherwise its properties were similar to those of the anhydride previously described (Found for the acid: C = 64.7; H = 2.9. Calc., C = 64.86; H = 2.7 per cent. Found for the anhydride: C = 69.4; H = 2.5. Calc., C = 69.1; H = 2.2 per cent.).

A comparison of the properties of these substances, especially their high melting points, with those of the corresponding acid and its anhydride made from the 1:2-dimethylantraquinone, as described immediately below, will be seen to prove this acid to be definitely the 2:3-dicarboxylic isomeride.

*Anthraquinone-1:2-dicarboxylic Acid and its Anhydride.*

The oxidation of the 1:2-dimethylantraquinone to its corresponding dicarboxylic acid was identical in method with that used for its isomeride, except that a temperature ten degrees lower was found advisable. The yield was again very good, a mass of fine yellow needles resulting, which, when crystallised from water, melted at about 265°, and when treated with acetic anhydride precipitated the corresponding anhydride, m. p. 320° (approx.); and in other respects the properties agreed with the recorded descriptions of this substance (Badische Anilin- & Soda-Fabrik,

Fr. Pat. 1910, 423986; Scholl and Schwinger, *Ber.*, 1911, 44, 2992; Scholl, D.R.-P. 1911, 241624; 1911, 243077). Since all the specimens previously described have been prepared by the breaking of a benzene ring attached in the 1 : 2 positions to an anthraquinone radicle, there can be no doubt that the carboxyl groups, and the methyl groups of the *o*-dimethylantraquinone from which it was prepared, are also in the 1 : 2 positions, as has already been explained.

*Dinaphthanthradiquinone (VIII).*

Dinaphthanthradiquinone (*lin.*-dibenz-1 : 4 : 5 : 8-anthradiquinone) has been successfully prepared from 2 : 3-dimethylantraquinone, thus independently confirming its 2 : 3 structure. The anhydride (10 grams) of the dicarboxylic acid prepared as described above, was warmed with benzene (1 litre) and aluminium chloride (10 grams) until the reaction started, and the mixture was cautiously heated throughout the progress of the reaction until hydrogen chloride ceased to be evolved. The reddish-yellow product was treated with water and hydrochloric acid, and was extracted with further portions of benzene. These extracts were evaporated and to their residue was added a yellow solid which had remained undissolved during the extractions. This product was then purified by precipitation from solution as an ammonium salt, but this purification of the acid led to so much difficulty that it has not as yet been completed, although the crude acid obtained was sufficiently pure to be dehydrated. It was heated gradually in twenty parts by weight of concentrated sulphuric acid to 110°, and maintained at that temperature for ten minutes, after which the black solution was filtered through glass wool, and diluted largely with water. The precipitate was washed with sodium hydroxide solution, and with water, then with a little glacial acetic acid. It was recrystallised from fresh glacial acetic acid, and finally was sublimed, when golden-yellow needles, stable up to, and melting at, a little more than 400°, were obtained. Independent proof was thus afforded of the 2 : 3 positions of the carboxyl groups in this molecule, as dinaphthanthradiquinone has already been proved to have a linear constitution (Philippi, *loc. cit.*; Mills and Mills, *loc. cit.*; Scholl and Seer, *loc. cit.*) (Found : C = 78.4; H = 2.9. Calc., C = 78.1; H = 2.96 per cent.).

*1 : 2-Phthaloylanthraquinone (VII).*

This substance was prepared in an exactly similar manner to that used in the case of its isomeric, the intermediate compound formed from the condensation of anthraquinone-1 : 2-dicarboxylic

acid with excess of benzene in the presence of aluminium chloride again not being isolated, owing to the difficulties experienced in its attempted purification. The crude product of the condensation was therefore partly purified as an ammonium salt and then immediately dehydrated by treatment with twenty parts by weight of concentrated sulphuric acid at a temperature of  $110^{\circ}$  during twenty minutes. The black liquid which resulted was filtered through glass wool, and poured into water, when a dark solid separated. This was washed with water and with dilute sodium hydroxide solution, and, after being dried, was crystallised from glacial acetic acid and boiling nitrobenzene. 1:2-Phthaloylanthraquinone was thus obtained as a greenish-yellow, acicular, crystalline product which decomposed before a definite melting point could be taken. Sublimation has not been successful, and combustion indicates that the material was not quite pure (Found: C = 78.6; H = 2.8. Calc., C = 78.1; H = 2.96 per cent.).

#### 2:3-Dimethylantracene.

Pure 2:3-dimethylanthraquinone was reduced by the method of Elbs and Eurich, and the product was found closely to resemble the dimethylantracene they describe (*Ber.*, 1887, **20**, 1361; *J. pr. Chem.*, 1890, [ii], **41**, 6), although the melting point was slightly higher, presumably owing to the absence of reduction products of the 1:2 series. This preparation of the anthracene from the purified 2:3-dimethylanthraquinone allows Elbs' argument as to the structure of these materials again to be applied as a probability, although the attempted reduction of the other isomeride has not as yet confirmed the formation of an inner ring such as is required by these considerations (Found: C = 92.9; H = 6.7. Calc., C = 93.2; H = 6.8 per cent.).

#### Anthracene-2:3-dicarboxylic Acid.

Pure anthraquinone-2:3-dicarboxylic acid was mixed with a large excess of zinc dust (six parts by weight) and dissolved in ammonia solution to which an equal volume of water had been added, 100 c.c. of this ammonia solution being used for every gram of the acid taken. The whole charge was then heated with constant shaking on the water-bath during two hours, when the pure anthracenedicarboxylic acid was precipitated from the hot filtered solution by the addition of hydrochloric acid, and was recrystallised from boiling alcohol. Small crystals were obtained which did not melt at  $350^{\circ}$ , but which were capable of sublimation to the anhydride as stated by Elbs

(Found : C = 71.9; H = 3.7. Calc., C = 72.2; H = 3.8 per cent.).

*The o-Dimethylantranols and Other Reduction Products.*

Limpricht (*Annalen*, 1900, **312**, 99) reduced 3:4-dimethylbenzoylbenzoic acid to the corresponding dimethylbenzylbenzoic acid, and he then dehydrated this, obtaining the dimethylantranol, which he classified as the 2:3-isomeride, giving as evidence that oxidation produced an *o*-dimethylantraquinone, m. p. 200°. From experiments so far carried out it would appear, however, that, just as in the case of the dehydration of the benzoylated acid, in which both isomerides result, so also in the dehydration of the benzylated acid both possible isomerides again result, and that the compounds described by Limpricht, including the final quinone, were 1:2- and 2:3-dimethylated isomeric mixtures, particularly rich, however, in the 2:3-form. The attempted isolation of the substances belonging to the 1:2 series in these reactions, and also the reduction products of the members of this 1:2 series mentioned previously, are at present under investigation by another member of this College.

In conclusion, the author wishes to take this opportunity of expressing his appreciation of the interest taken by Professor Smiles in the arguments put forward in this paper.

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[Received, July 22nd, 1921.]

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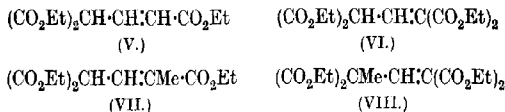
CLXXXIV.—*Experiments on the Synthesis of the Polyacetic Acids of Methane. Part III. Conditions Controlling Synthesis by the Cyanoacetic Ester Method—(continued).*

By CHRISTOPHER KELK INGOLD and EDWARD ARTHUR PERREN.

THE conditions which appear to govern the synthesis of the methanetriacetic acids by the interaction of ethyl sodiocyanoacetate either with halogen compounds or with the esters of unsaturated acids have been examined in some detail in a recent communication

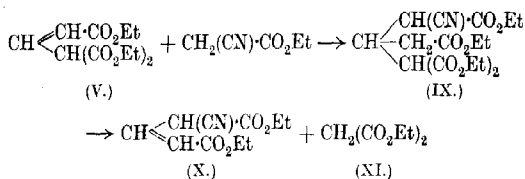


oxy- $\gamma$ -methylglutaconate (VII), and ethyl  $\alpha$ -dicarboxy- $\alpha$ -methylglutaconate (VIII):



All these substances readily reacted with ethyl sodiocyanoacetate, and no evidence was obtained of their possessing any tendency to pass into their normal modifications (the ester VIII, clearly, has no normal form) under the experimental conditions employed. Nevertheless, the products of these condensations, excepting in one instance in special circumstances (p. 1586), contained no trace of the expected derivatives of methanetriacetic acid, but consisted almost wholly of fission products formed from these substances by a remarkable decomposition having the character of a retrograde Michael reaction.

The ester V, for instance, gave initially a condensation product (IX), which then underwent complete fission into ethyl  $\alpha$ -cyano-glutaconate (X) and ethyl malonate (XI):



The products were purified and identified with some considerable care, the ethyl malonate, for instance, by its boiling point, by analysis, and by conversion into malonamide. Ethyl  $\alpha$ -cyano-glutaconate has been prepared both by Guthzeit and Eyssen (*J. pr. Chem.*, 1909, [ii], **80**, 41) and by Verkade (*K. Akad. Wetensch. Amsterdam*, 1919, **27**, 1132), whose descriptions closely agree with our own observations. The substance, however, was analysed and its identity fully confirmed by converting it into the crystalline ethyl derivative,  $\text{CO}_2\text{Et}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$  (XII), obtained by Guthzeit and Eyssen (*loc. cit.*, p. 44).

That the equations given above correctly represent the course of the reaction is, we believe, conclusively proved by the experiments described hereunder. In particular, the second reaction, involving as it does the elimination of ethyl malonate from a substance in which a number of substituted acetic acid residues

are attached to the same carbon atom, is typical of the decompositions described in this paper; and it may be stated at once that the general character of the determining conditions, so far as we have been able to discover them, appears to be concerned with the accumulation at the same carbon atom of several branched-chain acetic acid residues, for, whenever this accumulation oversteps a certain limit, one of the groups, usually the largest, will be eliminated from the molecule.

The ultimate cause of the reaction would therefore appear to be largely spatial in character and to be closely connected with the considerations recently put forward (this vol., p. 305, 951) relating to the distribution of groups of different volume around the methane carbon atom.

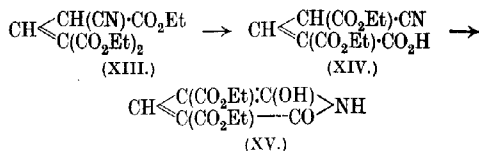
In extending the study of this reaction it was necessary in the first place to prove that it had some generality of application, and dicarboxyglutaconic ester (VI) was therefore investigated. This ester has one branched acetic acid chain more than ethyl *iso*-aconitate, and there should be an opportunity for two separate ethyl malonate residues to become eliminated from the original condensation product with ethyl cyanoacetate. Moreover, from what has been said it will be anticipated that, in view of the presence of the additional branched chain, it might be possible to observe some tendency, at least, towards the elimination of *both* ethyl malonate residues from the molecule.

The main products obtained by the action of ethyl sodiocyanoacetate on ethyl dicarboxyglutaconate, or rather on its very stable sodio-derivative (Conrad and Guthzeit, *Ber.*, 1882, **15**, 284), were ethyl malonate and a yellow oil, which, although it could not be purified by distillation, gave on analysis figures approximating to those required for the cyanocarboxyglutaconic ester (XIII). In reality its principal constituent was this ester, which was separated in the pure condition by regeneration from its monosodio-derivative, a yellow, sparingly soluble substance very similar in all essential respects to the sodio-compound of ethyl dicarboxyglutaconate first prepared by Conrad and Guthzeit.

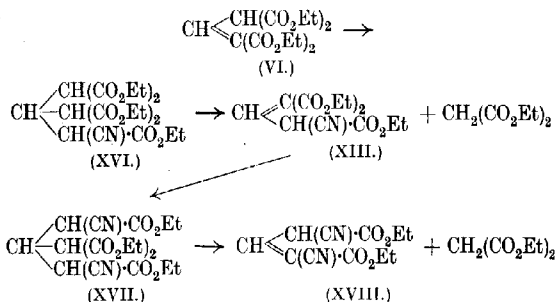
As an additional control on its constitution, the cyano-ester was subjected to regulated hydrolysis by hydrochloric acid, with which it reacted with extraordinary ease to form an acid cyano-ester (XIV). This, however, in the presence of the reagent, rapidly passed, by an internal rearrangement of a very familiar type (compare the formation of phthalimide from *o*-cyanobenzoic acid), into the well-known ester-imide of dicarboxyglutaconic acid (ethyl 6-hydroxy-2-keto- $\Delta^{3:5}$ -dihydropyridine-3:5-dicarboxylate, a form of ethyl 2:6-dihydroxynicotinate, XV) (Guthzeit, *Ber.*, 1893,



26, 2796; Errera, *Ber.*, 1898, **31**, 1243; Guthzeit and Eyssen, *loc. cit.*):



Besides ethyl  $\alpha$ -cyano- $\gamma$ -carboxyglutaconate and ethyl malonate, a small quantity of a crystalline material was isolated from the condensation product, and was identified as ethyl  $\alpha$ - $\gamma$ -dicyanoglutaconate (Errera, *Gazzetta*, 1898, [ii], **27**, 393; Ruhemann and Browning, T., 1898, **65**, 280) (XVIII). The same substance was produced when ethyl cyanocarboxyglutaconate was treated with ethyl sodiocyanoacetate, and its formation in the original condensation must therefore have involved the production and subsequent fission of two methanetriacetic acid derivatives (XVI and XVII) by a series of direct and retrograde Michael condensations:

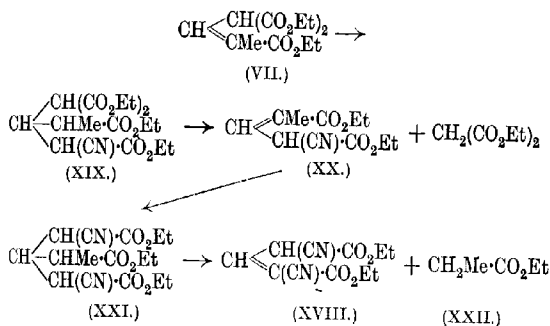


This therefore is a noteworthy extension of the reaction previously described. However, the yield of ethyl dicyanoglutaconate was never large \* and it was not found possible to distinguish satisfactorily between the first and the second molecule of ethyl malonate eliminated during the successive fission reactions. Moreover, owing to the slight solubility in cold alcohol of the sodio-derivatives of ethyl cyanocarboxyglutaconate and ethyl dicarboxyglutaconate, it was impossible to conduct the series of changes at a low temperature (compare below); for this reason, and also because

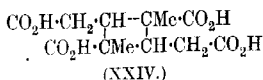
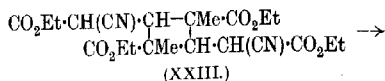
\* Reference to two papers by Verkade (*K. Akad. Wetensch. Amsterdam*, 1915, **24**, 865; 1919, **27**, 1130) on ethyl cyanoglutaconate will suggest possible reasons for this.

fractional distillation as a means of separating the products was impracticable, experiments on the isolation of the intermediate methanetriacetic acid derivatives met with no success.

Therefore we turned to another example, namely, that afforded by the condensation of ethyl  $\alpha$ -cyano- $\gamma$ -methylglutaconate (VII). Here the two substituted acetic acid residues, which, by analogy, one would expect to find as elimination products of the fission reactions, are not identical; one should be eliminated as ethyl malonate and the other as ethyl propionate, and by isolating and identifying these it should be possible to follow in detail the successive stages of the process. Actually, although the main products under the usual experimental conditions were ethyl  $\alpha$ -cyano- $\gamma$ -methylglutaconate (XX) and ethyl malonate, the quantity of ethyl dicyanoglutaconate (XVIII) produced was very considerable if the time allowed were prolonged; and, moreover, it was found possible in this case to separate and satisfactorily to identify ethyl propionate, the second of the eliminated residues. Further, by conducting the condensation at a low temperature, the later stages of the process became arrested to such a degree as to render practicable the isolation of the  $\omega$ -methylmethane-iacetic acid derivative (XIX) originally formed. The complete series of changes is therefore as follows:

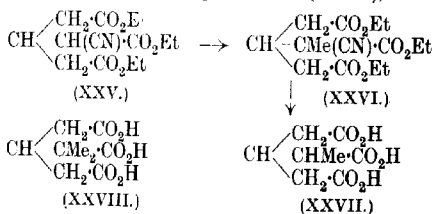


Perhaps it should be added here that the course pursued by the condensation was in reality rather more complicated than this, owing to the extraordinary tendency possessed by the cyano-ethylglutaconic ester to pass into a crystalline cyano-ester (m. p.  $17^\circ$ ), which may provisionally be represented by the formula XXIII; and, on hydrolysis by means of acids, it yielded a tetrabasic acid (m. p.  $242^\circ$ ), which, there is good reason to believe, is an acid (XXIV) belonging to the cyclobutane series:



The formation of these substances is, of course, part of the wider question, discussed in a recent paper by one of us (this vol., p. 951), relating to the ease of formation and the stability of *cyclobutane* derivatives. Further papers on this and allied subjects will shortly be presented to the Society; in the meantime, with regard to the example under consideration, it may merely be stated that the reaction leading to the ester, m. p. 87°, appears to be favoured by the use of a slight deficit of sodium ethoxide, and that in these circumstances its formation often occurs to such an extent as to suppress almost completely all products formed (compare the scheme outlined above) subsequently to the cyano-ester (XX).

All products of the condensation were carefully identified, the liquids, after analysis, being converted into crystalline derivatives which were then directly compared with authentic specimens. Ethyl propionate and ethyl malonate were converted into propionamide and malonamide respectively. The cyanomethylglutaconic ester (XX) was hydrolysed to  $\alpha$ -methylglutaconic acid, which proved to be identical with a specimen of this acid kindly lent by Prof. J. F. Thorpe. The methanetriacetic acid derivative (XIX), on hydrolysis, gave  $\omega$ -methylmethanetriacetic acid (XXVII), which, as a degradation product of quinine (Skraup, *Monatsh.*, 1900, 21, 879) and on account of its close relationship with *iso*-camphoric acid (XXVIII), is an acid of considerable interest. We have synthesised it for comparison with the acid obtained from the condensation product by a method which should leave no doubt as to its constitution: ethyl  $\omega$ -cyanomethanetriacetate (XXV) (Ingold, *loc. cit.*) was converted into its sodio-derivative and then methylated; the methylated ester (XXVI),



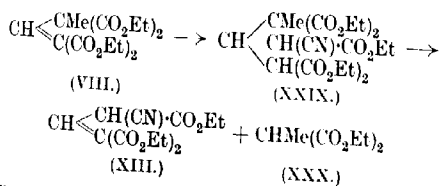
on hydrolysis by sulphuric acid, yielded  $\omega$ -methylmethanetriacetic

acid identical in all respects with the substance obtained from the products of the condensation described above.

From what has been said it might at first sight appear remarkable that the esters XXV and XXVI should be, as apparently they are, quite stable towards boiling alcoholic sodium ethoxide solution. If, however, their formulae be compared with those of the methanetriacetic acid derivatives previously mentioned (IX, XVI, XVII, XIX, and XXI), it will be observed that each of the latter contains *at least two* branched acetic acid chains, and it would certainly seem, from the present investigation, to be a condition necessary for instability that at least two of the three acetic acid chains attached to the methane carbon atom should bear substituent groups.

That some such limit should exist is in full harmony with the spatial view of the matter, which, for reasons that cannot here be fully entered into, we have been led to adopt. There must be certain definite, necessary, and *sufficient* conditions, which cannot be traced or even adumbrated in a restricted investigation such as this. The question of definition requires experiments based on a wider plan, and some of these have now been commenced. By this means, it is hoped, the problem may be explored along some at least of its principal directions, but in the meantime it has seemed desirable to obtain some confirmation of a general character, at least so far as methanepolyacetic acid derivatives are concerned, by examining the case of fission of a methanetriacetic ester containing as many substituents as could conveniently be introduced.

With this object in view the condensation of ethyl  $\alpha$ -dicarboxy- $\alpha$ -methylglutaconate (VIII) with ethyl sodiocyanoacetate was investigated, and it was found, as anticipated, that the two substances reacted at the ordinary temperature with remarkable ease, yielding in the course of a few hours almost theoretical amounts of ethyl  $\alpha$ -cyano- $\gamma$ -carboxyglutaconate (XIII) and ethyl methylmalonate (XXX):



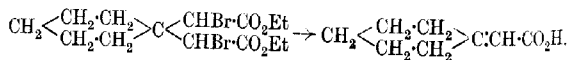
The former was identified by analysis and by conversion into the ester-imide (XV), and the latter by analysis and conversion into the amide. The intermediate methanetriacetic acid derivative

(XXIX) must have been very short-lived, for, in spite of the low temperature at which the condensation was carried out, no trace of it could be isolated.

When the nature of these condensations had been elucidated, the literature was searched for accounts of reactions having a similar character. The only example, however, which could be found of a reaction apparently involving a retrograde Michael condensation is the observation by Kötze and Zörnig (*J. pr. Chem.*, 1906, [ii], 74, 427, *Anmerkung*) that ethyl benzylmalonate can be isolated from the product formed when ethyl sodiomalonate is allowed to react with ethyl  $\alpha$ -dicarboxy- $\alpha$ -methylglutaconate. The mechanism of this reaction is doubtless analogous to that of the condensations described above, although Kötze and Zörnig do not appear to have examined their product as closely as is desirable for the purpose of establishing the matter definitely.

There are, however, on record a very large number of reactions in which the operation of the factors governing the phenomena discussed in the present paper is to be traced. Thus Kötze and Zörnig carried out many condensations between chloroform and the sodium compounds of various ketones, esters, and nitriles (for example, deoxybenzoin, ethyl methylmalonate, malononitrile) with the object of preparing compounds in which three organic residues had become attached to the methane carbon atom supplied by the chloroform. In no case, however, was a product of this constitution obtained, the sodium compound employed invariably reacting after the manner of ethyl sodiomalonate, if that were possible, or, in the case of compounds lacking the hydrogen atom necessary for this type of condensation, in such a way as to leave one of the halogen atoms of the chloroform molecule undisturbed. The reason for this is not difficult to discover; for in all the cases investigated the desired condensation products, had they been obtained, would have contained three branched acetic acid chains, a condition of the molecule incompatible with stability.

An illuminating instance of the elimination of a substituted acetic acid residue in a totally different type of reaction is that furnished by the conversion of ethyl  $\alpha\alpha'$ -dibromocyclohexane-1:1-diacetate to cyclohexylideneacetic acid by hydrolysis (Beesley, Ingold, and Thorpe, T., 1915, 107, 1080):



No reaction of a similar character has been observed with the corresponding derivative of  $\beta\beta$ -dimethylglutaric acid, namely, the bromo-ester,  $\text{CMe}_2(\text{CHBr} \cdot \text{CO}_2\text{Et})_2$ , a fact which has been

attributed (*loc. cit.*) to the *gem*-methyl groups together occupying less of the space surrounding the quaternary carbon atom than the  $C_7H_{10}$  residue in the corresponding cyclic compound. The consideration of this and many similar instances, some of which occur in the literature of triphenylmethyl and its analogues, many in that which relates to the Michael and Knoevenagel condensations, leads, we consider inevitably, to the conclusion that, as suggested on p. 1585, spatial causes are at the root of all these phenomena, and amongst them the reactions described in this paper.

Reference to certain new derivatives of 6-ethoxy-2-pyrone, which were obtained incidentally in the course of the research, will be found at the end of the experimental portion.

## EXPERIMENTAL.

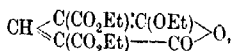
### (A) Preparation of $\alpha$ -Substituted Glutaconic Esters.

*Ethyl  $\alpha$ -Dicarboxylglutaconate* (VI).—The sodium compound of this ester was prepared by Conrad and Guthzeit's method (*Ber.*, 1882, 15, 281), certain modifications, however, being introduced with the object of improving the yield. Coutelle, who made a detailed study of the reaction, states (*J. pr. Chem.*, 1906, [ii], 73, 49) that the maximal yield is 41–42 per cent. of the theoretical, but by the following method it is possible to obtain 60 per cent. with certainty.

Ethyl malonate (160 grams) was added to a solution of sodium ethoxide prepared by dissolving 46 grams of sodium in 1 litre of absolute ethyl alcohol. When the temperature was between 30° and 35°, chloroform (60 grams) was poured in and the mixture allowed to remain until the violent ebullition caused by the heat developed in the reaction had subsided. The mixture was then heated for half an hour on a water-bath with a further quantity (20 grams) of chloroform and filtered while still hot. The yellow sodium compound (80 grams) separated from the filtrate on cooling and a further 25 grams were obtained by concentrating the mother-liquors to about one-sixth of their bulk.

The free ester was prepared from the sodium compound in the way recommended by Conrad and Guthzeit (*loc. cit.*).

*Ethyl  $\alpha$ -Carboxylglutaconate* (*Ethyl isoaconitate*, V).—For the preparation of ethyl *isoaconitate* ethyl dicarboxylglutaconate was first converted by heating at 200° into ethyl 6-ethoxy-2-pyrone-3:5-dicarboxylate,



which was then hydrolysed to the *isoaconitate* by means of cold 2.5 per cent. aqueous sodium hydroxide, as recommended by Gùthzeit and Dessel (*Ber.*, 1889, **22**, 1413).

In working up large quantities it was found desirable to purify the pyrone carefully by crystallisation from ether, since when this was done it was unnecessary to distil the ethyl *isoaconitate*, an operation which was often troublesome unless carried out with small amounts of material.

*Ethyl  $\alpha$ -Dicarboxy- $\alpha$ -methylglutaconate* (VIII).—This substance was prepared by methylating the yellow sodium compound of ethyl dicarboxyglutaconate in the manner described by Thole and Thorpe (*T.*, 1911, **99**, 2197).

*Ethyl  $\alpha$ -carboxy- $\gamma$ -methylglutaconate* (VII) was obtained from ethyl dicarboxymethylglutaconate by the action of sodium ethoxide (Thole and Thorpe, *loc. cit.*).

(B) *Condensation of Ethyl  $\alpha$ -Carboxyglutaconate (Ethyl isoAconitate) with Ethyl Cyanoacetate. Isolation of Ethyl  $\alpha$ -Cyanoglutaconate and Ethyl Malonate.*

Ethyl *isoaconitate* (26 grams; 1 mol.) was mixed with a suspension in absolute ethyl alcohol of ethyl sodiocyanoacetate prepared from 4.8 grams (slightly more than two atoms) of sodium, 75 c.c. of ethyl alcohol, and 22.6 grams (2 mols.) of ethyl cyanoacetate. The mixture, which at once became yellow owing to the formation of the sodium compound of ethyl *isoaconitate*, was allowed to remain for a short time at room temperature, and was then heated on the steam-bath for fifteen hours, at the end of which time most of the alcohol was distilled off and the residue mixed with water. The precipitated oil was extracted with ether, the acid substances remaining in the aqueous solution being recovered by acidifying and again extracting.

*Ethyl Malonate* (XI).

On distillation under diminished pressure, the neutral ester was found to consist chiefly of ethyl malonate, six grams of which were obtained in a pure condition, b. p. 104°/30 mm., by a second distillation. Its identity was proved by analysis (Found: C = 52.3; H = 7.3. Calc., C = 52.5; H = 7.5 per cent.), and by converting it into malonamide, which was compared with a known specimen and further identified by a mixed melting point determination.

The alcoholic distillate (above) was saturated with ammonia, and, two days later, mixed with concentrated aqueous ammonia.

The mixture was kept at room temperature for a further period of two days and then evaporated in a vacuum. The small residue proved to be almost pure malonamide, and, in spite of a careful search, no trace of acetamide could be detected (contrast section D).

The less volatile portion of the neutral fraction was very small in amount, but it yielded two crystalline substances, m. p.  $116^{\circ}$  and  $179^{\circ}$  respectively, which, however, were not obtained in quantities sufficient for further investigation.

*Ethyl  $\alpha$ -Cyanoglutaconate (X).*

The acid extract, on evaporation, left a pale yellow, viscous oil, which could not be distilled; but which was found to consist essentially of ethyl cyanoglutaconate. The method of purification finally adopted was as follows. The oil was mixed with ether and shaken, first with water, and then for several hours with an aqueous suspension of precipitated calcium carbonate. The ester recovered by drying and evaporating the ethereal solution was converted, by mixing with an approximately equivalent quantity of ethyl-alcoholic sodium ethoxide, into its sodio-derivative, which was precipitated by adding ether, collected, and decomposed by means of cold dilute hydrochloric acid. The liberated ester, which consisted of pure ethyl cyanoglutaconate, was extracted by means of pure ether, the last traces of which were expelled in an evacuated desiccator (Found: C = 56.5; H = 6.2; N = 7.0. Calc., C = 56.8; H = 6.2; N = 6.7 per cent.).

The ester corresponded closely in its properties with the substance described by Guthzeit and Eyssen (*loc. cit.*). However, in order to identify it with certainty, it was converted by ethylation, by means of alcoholic sodium ethoxide and ethyl iodide, into ethyl  $\alpha$ -cyano- $\alpha$ -ethylglutaconate (XII) (Found: C = 60.4; H = 7.4. Calc., C = 60.2; H = 7.1 per cent.), which had the melting point ( $79^{\circ}$ ) and "glass-wool-like" appearance mentioned by those authors.

(C) *Condensation of Ethyl  $\alpha$ -Dicarboxyglutaconate with Ethyl Cyanoacetate: Isolation of Ethyl  $\alpha$ -Cyano- $\gamma$ -carboxyglutaconate, Ethyl  $\alpha$ - $\gamma$ -Dicyanoglutaconate, and Ethyl Malonate.*

Ethyl cyanoacetate (22.6 grams; 2 mols.) was mixed with a solution of sodium ethoxide prepared by dissolving 4.6 grams of sodium (one atom) in 60 grams of absolute ethyl alcohol. When the precipitation of ethyl sodiocyanoacetate appeared to be complete, 36 grams (1 mol.) of the recrystallised and finely ground



sodium compound of ethyl dicarboxyglutaconate (section A) were added and the mixture was heated with frequent shaking on a steam-bath for a period of eighteen hours, during which the sodium compound gradually dissolved and another much less strongly coloured substance separated from the brown solution. The product was poured into dilute hydrochloric acid and extracted with ether, the acidic substances being removed from the extract by washing with dilute aqueous sodium carbonate solution and recovered from the washings by acidifying and again extracting.

*Ethyl Malonate (XI).*

Most of the neutral ester boiled at 90–105°/10 mm., and this fraction on redistillation yielded pure ethyl malonate (Found: C = 52.4; H = 7.5. Calc., C = 52.5; H = 7.4 per cent.), which was satisfactorily identified by converting it into malonamide and comparing this with a genuine specimen.

A very small quantity of material boiling in the neighbourhood of 200°/10 mm. was also collected, and this, on keeping for a few days, partly solidified. The crystals were drained on porous porcelain, washed with ether, and recrystallised twice from this solvent. They separated in long needles, m. p. 93–94°, and must have consisted of ethyl 6-ethoxy-2-pyrone-3:5-dicarboxylate (Found: C = 54.7; H = 5.6. Calc., C = 54.9; H = 5.6 per cent.), although at the time none of this material was at hand for comparison. On keeping, the crystals partly liquefied, a property which the pyrone also possesses.

*Ethyl  $\alpha$ -Cyano- $\gamma$ -carboxyglutaconate (XIII).*

The acid extract (above), after being dried with sodium sulphate (calcium chloride caused the precipitation of a yellow calcium salt) and evaporated, left a yellow, viscous oil, which could not be distilled, but consisted chiefly of ethyl  $\alpha$ -cyano- $\gamma$ -carboxyglutaconate and a small quantity of ethyl  $\alpha\gamma$ -dicyanoglutaconate, crystals of which could sometimes be obtained from it by keeping. The crude oil was triturated with cold dilute aqueous sodium hydroxide, which converted it into a biscuit-coloured mixture of sparingly soluble sodium compounds. These were collected, washed with hot water, and decomposed by cold dilute hydrochloric acid, the ester liberated being at once extracted with benzene, and the extract dried by shaking with sodium sulphate and evaporated at room temperature in a vacuum. The ethyl  $\alpha$ -cyano- $\gamma$ -carboxyglutaconate thus obtained was a pale yellow oil, giving with aqueous

alcoholic ferric chloride a deep crimson colour (Found: C = 55.4; H = 6.2; N = 5.4.  $C_{13}H_{17}O_6N$  requires C = 55.1; H = 6.0; N = 5.0 per cent.).

The ester appears to have been obtained previously by Errera (*Ber.*, 1898, **31**, 1243) by the action of ethyl cyanoacetate on ethyl ethoxymethylenemalonate, but no steps were taken to purify the product and no analysis is quoted.

In order to obtain a further check on the constitution of the substance, it was subjected to regulated hydrolysis by hydrochloric acid. It dissolved completely in the cold concentrated acid, but on warming an oil separated. This oil was, apparently, the acid ester (XIV), for on shaking for a few minutes with the hot concentrated acid it was quickly converted into a sparingly soluble, crystalline substance, which melted at  $199^\circ$  and had all the characteristics of ethyl 6-hydroxy-2-keto- $\Delta^{3:5}$ -dihydropyridine (XV) (a modification of ethyl 2:6-dihydroxynicotinate, and of the imide-ester of dicarboxyglutaconic acid. Compare Guthzeit, *Ber.*, 1893, **26**, 2796; Errera, *loc. cit.*, and Guthzeit and Eysen, *loc. cit.*).

The *sodio*-compound, obtained in the course of the above separation, and prepared from the pure cyano-ester by treatment with sodium hydroxide, was a pale yellow, crystalline substance sparingly soluble in water and alcohol (Found: Na = 7.2.  $C_{13}H_{15}O_6NNa$  requires Na = 7.5 per cent.).

The *calcio*-derivative, a yellow, crystalline powder, was prepared from the cyano-ester, aqueous calcium chloride, and ammonium hydroxide (Found: Ca = 6.3.  $C_{26}H_{32}O_{12}N_2Ca$  requires Ca = 6.6 per cent.).

#### *Ethyl $\alpha\gamma$ -Dicyanoglutaconate* (XVIII).

The washings from the foregoing sodium compounds, on keeping, deposited an almost colourless sodium compound, which, on trituration with dilute hydrochloric acid, yielded a bright yellow, crystalline substance. This was identified as ethyl dicyanoglutaconate (Errera, *Gazzetta*, 1898, [ii], **27**, 393; Ruhemann and Browning, *loc. cit.*) by its melting point,  $184$ – $186^\circ$ , nitrogen content (Found: N = 11.6. Calc., N = 11.8 per cent.), and by direct comparison with an authentic specimen.

*Formation of Ethyl  $\alpha\gamma$ -Dicyanoglutaconate from Ethyl  $\alpha$ -Cyano- $\gamma$ -carboxyglutaconate and Ethyl Cyanoacetate.*

Ethyl cyanoacetate (2.3 grams) and ethyl sodio- $\alpha$ -cyano- $\gamma$ -carboxyglutaconate (3 grams) were successively added to a solution

of sodium ethoxide prepared from 0.23 gram of sodium and 6 grams of absolute ethyl alcohol. The mixture was heated on a water-bath for twenty-four hours and then evaporated, the residue being treated with dilute hydrochloric acid and the precipitated oil divided into neutral and acid fractions by ether and sodium carbonate in the usual way. The neutral fraction appeared to consist of ethyl malonate, but the quantity was very small, and it was therefore not identified with certainty. The acid fraction was separated into its constituents by converting it into sodium compounds and extracting these with hot water as described on p. 1594, and in this way a small amount of ethyl  $\alpha$ , $\gamma$ -dicyanoglutaconate, as well as a considerable quantity of unchanged ethyl  $\alpha$ -cyano- $\gamma$ -carboxyglutaconate, were isolated in the pure condition.

(D) *Condensation of Ethyl  $\alpha$ -Carboxy- $\gamma$ -methylglutaconate with Ethyl Cyanoacetate: Isolation of  $\omega$ -Methylmethanetriacetic Acid, Ethyl  $\alpha$ -Cyano- $\gamma$ -methylglutaconate, Ethyl  $\alpha$ , $\gamma$ -Dicyanoglutaconate, Ethyl Malonate, and Ethyl Propionate.*

In carrying out this condensation it was found necessary to use a slight excess of sodium ethoxide in order to avoid the formation of the cyclobutane derivative (XXIII).

Ethyl cyanoacetate (22.6 grams; 2 mols.) and ethyl  $\alpha$ -carboxy- $\gamma$ -methylglutaconate (27.2 grams; 1 mol.) (section A) were added in succession to a solution of sodium ethoxide prepared by dissolving sodium (5 grams; 2.1 atoms) in absolute ethyl alcohol (70 c.c.). The mixture was heated for thirty hours and then distilled until the temperature reached 100°.

*Ethyl Propionate (XXII).*

The distillate contained a quantity of ethyl propionate, which, however, could not be separated from the large excess of ethyl alcohol accompanying it. It was therefore converted into the amide by saturating the alcoholic solution with ammonia and, after some hours, adding concentrated aqueous ammonia. The amide thus obtained was recrystallised from a small amount of water and identified as propionamide by analysis (Found: C = 49.3; H = 9.7; N = 19.4. Calc., C = 49.3; H = 9.6; N = 19.2 per cent.), by its m. p. (79°) and characteristic appearance, and by direct comparison with a specimen prepared from an authentic sample of ethyl propionate.

*Ethyl Malonate (XI).*

The pasty residue from the distillation (p. 1596) was mixed with water and extracted with ether. The oil thus obtained boiled almost entirely between  $90^{\circ}$  and  $100^{\circ}/15$  mm., and on redistillation at atmospheric pressure yielded 10 grams of pure ethyl malonate. Found: C = 52.4; H = 7.5. Calc., C = 52.5; H = 7.5 per cent.), which was identified, as before, by conversion into malonamide.

A further quantity was obtained by esterifying, by means of ethyl alcohol and sulphuric acid, the acid substances recovered from the alkaline solution from which the sodio-derivative of ethyl dicyanoglutaconate had crystallised (below), the neutral esterification product consisting of about equal parts of ethyl malonate and ethyl  $\alpha$ -carboxy- $\gamma$ -methylglutaconate, which were easily separated by distillation.

*Ethyl  $\alpha$ -Cyano- $\gamma$ -methylglutaconate (XX).*

The alkaline solution from which the ethyl malonate was extracted was acidified and again extracted with ether, the products being separated into acid and quasi-acid fractions by washing with 10 per cent. aqueous sodium carbonate solution. The quasi-acid fraction boiled at  $160$ — $170^{\circ}/15$  mm., and consisted almost entirely of ethyl  $\alpha$ -cyano- $\gamma$ -methylglutaconate, 14 grams of which were obtained on redistillation as a colourless oil, b. p.  $160^{\circ}/15$  mm. (Found: C = 58.3; H = 6.9; N = 6.5.  $C_{11}H_{15}O_4N$  requires C = 58.6; H = 6.7; N = 6.2 per cent.). It gave a deep reddish-brown colour with aqueous-alcoholic ferric chloride.

As mentioned above, a further quantity of the substance was obtained by esterifying the acid products.

In order to confirm its constitution, the ester was hydrolysed by boiling with 50 per cent. sulphuric acid. The product, extracted by ether and crystallised from water, was identified as  $\alpha$ -methylglutaconic acid by analysis (Found: C = 50.1; H = 5.7. Calc., C = 50.0; H = 5.5 per cent.), by direct comparison with a genuine specimen, and by a mixed melting-point determination.

*Ethyl  $\alpha$ , $\gamma$ -Dicyanoglutaconate (XVIII).*

The sodium carbonate washings (above) quickly deposited a very pale brown, crystalline sodium compound, which, after purification by recrystallisation from water or alcohol, melted at  $263$ — $265^{\circ}$  and evidently consisted of ethyl sodiodicyanoglutaconate (Found: Na = 8.9. Calc., Na = 8.9 per cent.).

The free dicyano-ester, prepared from the sodium compound, was identified by comparison with a known specimen and by analysis (Found: C = 54.5; H = 5.4; N = 11.7. Calc., C = 55.9; H = 5.1; N = 11.9 per cent.), the results of which, although not agreeing very closely with the theoretical values, are similar to the figures obtained by Errera (*loc. cit.*) and by Ruhemann and Browning (*loc. cit.*), and are to be attributed to the well-known tendency of the substance to retain small amounts of water with great persistency.

*Formation of Ethyl  $\alpha$ -Dicyanoglutaconate from Ethyl  $\alpha$ -Cyano- $\gamma$ -methylglutaconate and Ethyl Cyanoacetate.*

Ethyl  $\alpha$ -cyano- $\gamma$ -methylglutaconate was heated with an alcoholic solution containing two molecular proportions of ethyl sodio-cyanoacetate. Although an excess of sodium ethoxide was present, a considerable amount of conversion into the cyclobutane derivative (XXIII) occurred. However, on dividing the product into neutral, quasi-acid, and acid portions in the manner previously described, this became separated from the dicyano-ester, which was isolated and identified as in the preceding instance.

*Formation of Derivatives of  $\omega$ -Methylmethanetriacetic Acid.*

In order to isolate derivatives of  $\omega$ -methylmethanetriacetic acid from the product of condensation of  $\alpha$ -cyano- $\gamma$ -methylglutaconic acid with ethyl sodiocyanoacetate, it was necessary to carry out the condensation entirely at room temperature. The reaction mixture, prepared as described on p. 1596, was therefore allowed to remain with occasional shaking for twenty-four hours at the ordinary temperature, and was then mixed with water and separated by means of ether and aqueous sodium carbonate into neutral, quasi-acid, and acid portions.

The neutral fraction on distillation yielded ethyl malonate and a small amount of a viscous liquid boiling in the neighbourhood of 200°/10 mm.

The quasi-acid fraction consisted almost entirely of ethyl  $\alpha$ -cyano- $\gamma$ -methylglutaconate, although a small amount of a similar fraction of high b. p. was separated from it.

The acid fraction contained no trace of ethyl  $\alpha$ -dicyanoglutaconate (compare section E), but when esterified and distilled gave the substance of high b. p. along with ethyl malonate and an intermediate fraction of indefinite boiling point.

The less volatile substance obtained in all these ways consisted

apparently of ethyl  $\omega$ -cyano- $\omega'$ -carboxy- $\omega''$ -methylmethanetriacetate XIX), for on hydrolysis by 50 per cent. sulphuric acid (compare p. 1600) it yielded  $\omega$ -methylmethanetriacetic acid (Found: C = 46.6; H = 6.0.  $C_8H_{12}O_6$  requires C = 47.0; H = 5.9 per cent.), which, after crystallisation from ethyl acetate, melted at 136–137° and was identical in all respects with the acid synthesised (section F) or comparison.

E) *Condensation of Ethyl  $\alpha$ -Dicarboxy- $\alpha$ -methylglutaconate with Ethyl Cyanoacetate: Isolation of Ethyl Methylmalonate and Ethyl  $\alpha$ -Cyano- $\gamma$ -carboxyglutaconate.*

Ethyl  $\alpha$ -dicyano- $\alpha$ -methylglutaconate (1 mol.) (section A) was condensed with ethyl sodiocyanoacetate (2 mols.) as in the preceding instances, excepting that, as in this case the reaction proceeded with extraordinary ease, the mixture was kept at room temperature for two hours only, and was then worked up for the products, which were separated into neutral and acid portions by means of ether and sodium carbonate.

*Ethyl Methylmalonate (XXX).*

Almost the whole of the neutral product distilled in the neighbourhood of 100°/10 mm., and on redistillation at atmospheric pressure boiled constantly at 195°. That this consisted of pure ethyl methylmalonate was proved by analysis (Found: C = 55.2; H = 8.0. Calc., C = 55.2; H = 8.0 per cent.), and by conversion into methylmalonamide, which was obtained in good yield and identified with an authentic specimen.

The amide contained no admixed malonamide, and, therefore, the reaction product could have contained no ethyl malonate (see below).

*Ethyl  $\alpha$ -Cyano- $\gamma$ -carboxyglutaconate (XIII).*

This substance (Found: C = 55.6; H = 6.3. Calc., C = 55.1; H = 6.0 per cent.) was isolated from the acid product of the condensation in the manner described in connexion with the previous reaction (section C) in which it was obtained, and was identified by means of its characteristic sodium derivative (Found: Na = 7.3. Calc., Na = 7.5 per cent.) and by conversion into the imide (XV) by boiling with hydrochloric acid.

No ethyl  $\alpha$ -dicyanoglutaconate was isolated from this condensation (compare that described on p. 1596), and it would appear

that the formation of this substance by the action of ethyl sodio-cyanoacetate on compounds such as ethyl  $\alpha$ -cyano- $\gamma$ -methylglutaconate and ethyl  $\alpha$ -cyano- $\gamma$ -carboxyglutaconate requires a higher temperature than that of the room.

(F) *Preparation of  $\omega$ -Methylmethanetriacetic Acid from Ethyl  $\omega$ -Cyanomethanetriacetate.*

These experiments were carried out in order to obtain a specimen of  $\omega$ -methylmethanetriacetic acid for comparison with the acid obtained in the condensation described in section D. The starting material, ethyl  $\omega$ -cyanomethanetriacetate, was prepared by the method described in a recent communication (Ingold, this vol., p. 352).

*Ethyl  $\omega$ -Cyano- $\omega$ -methylmethanetriacetate (XXVI).*

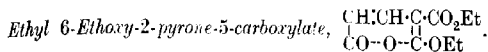
Ethyl  $\omega$ -cyanomethanetriacetate was mixed with an alcoholic solution containing one equivalent of sodium ethoxide, and then with a slight excess of methyl iodide. The solution was boiled until neutral to moistened litmus, and the esters were isolated by adding water and extracting with ether. *Ethyl  $\omega$ -cyano- $\omega$ -methylmethanetriacetate* was obtained, by distillation under diminished pressure, as a colourless, viscous oil, b. p. 206–208°/12 mm. (Found: C = 57.6; H = 7.5.  $C_{15}H_{23}O_6N$  requires C = 57.5; H = 7.3 per cent.).

*$\omega$ -Methylmethanetriacetic Acid (XXVII).*

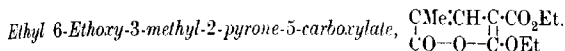
A mixture of the pure methylated cyano-ester and an equal volume of cold concentrated sulphuric acid was diluted, after twelve hours' keeping, with sufficient water to cause a slight precipitation of oil, and then heated for seven hours on a sand-bath, a further quantity of water being added and the reflux condenser removed towards the end of this period after the evolution of carbon dioxide had ceased. The solution was cooled, saturated with ammonium sulphate, and extracted repeatedly with ether. The colourless syrup which remained on drying and evaporating the ether immediately solidified with evolution of heat on touching with a glass rod. The acid was crystallised from ethyl acetate for analysis; it separated in small, dense prisms, m. p. 137–138° [Found: C = 46.9; H = 6.0. M (by titration) = 203.1. Calc., C = 47.0; H = 5.9 per cent.; M = 204].

(G) *Note on some Derivatives of 6-Ethoxy-2-pyrone.*

The following compounds were obtained incidentally during the preparation of some of the materials required for this research. They have not been investigated in detail, but their constitutions appear to follow from their modes of formation, and it has been thought desirable to append a brief description.



Ethyl *isocaconitate* is apt to decompose on distillation and on one occasion the pyrone was isolated from the dark residue obtained in this manner. It was purified by rubbing with ether and crystallisation from ethyl acetate, from which it separated in needles, m. p.  $132^\circ$  (Found: C = 56.7; H = 5.3.  $\text{C}_{10}\text{H}_{12}\text{O}_5$  requires C = 56.6; H = 5.6 per cent.). With aqueous alcoholic ferric chloride it formed a deep crimson coloration.



This compound was invariably formed to some extent when large quantities of ethyl  $\alpha$ -carboxy- $\gamma$ -methylglutaconate were distilled at a time, and occasionally it crystallised from the distillate. The material obtained in this way was purified for analysis by crystallisation from ethyl acetate. It separated in colourless, transparent strips or blades, usually long and very thin, a typical size being 20 mm.  $\times$  1 mm.  $\times$  0.05 mm. (Found: C = 58.1; H = 6.1.  $\text{C}_{11}\text{H}_{14}\text{O}_5$  requires C = 58.3; H = 6.4 per cent. M, by the cryoscopic method in benzene, = 224. Calc., M = 226). It melted at  $94^\circ$  and gave no distinct coloration with ferric chloride.

We desire to express our gratitude to Professor J. F. Thorpe for his interest in these experiments and for much very valuable advice; also to the Chemical Society for a grant from their Research Fund which has greatly facilitated the work.

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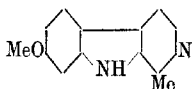
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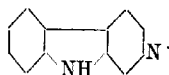
CLXXXV.—*Harmine and Harmaline. Part V. The  
Synthesis of Norharman.*

By WILLIAM OGILVY KERMACK, WILLIAM HENRY PERKIN, jun.,  
and ROBERT ROBINSON.

IN Parts III and IV of this research (T., 1919, **115**, 933 *et seq.*) evidence was brought forward and discussed which seemed to leave little doubt that harmine has the constitution I, whilst two possibilities remain for harmaline (dihydroharmine), the decision between which can only be made after the accumulation of further data.



(I.)



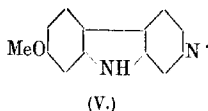
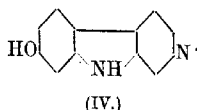
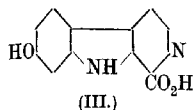
(II.)

It appeared desirable, however, to support the strong analytical arguments by synthesis, and especially so in view of the fact that the fused pyridine-pyrrole nucleus type represents a domain of organic chemistry which has hitherto remained almost unexplored. In planning the synthetic investigation we have had always in view the systematic study of the methods available for the preparation of the more characteristic members of this group of bases, and accordingly in the first instance chose to attack the problem of the synthesis of 4-carboline (II), which can be regarded as the true parent substance of harmine and harmaline.

Harmine is methylmethoxy-4-carboline, and since the compounds obtained by elimination of the methyl and methoxy-groups from harmine are respectively termed norharminine and harman, it is clear that 4-carboline may also be called norharman in order to emphasise its relation with the harmala group of alkaloids.

Two methods have now been devised for the degradation of harmine to norharman, and the first of these arose from the investigation of harmolic acid, which O. Fischer (*Ber.*, 1889, **22**, 642) produced by the alkali fusion of harmo., the phenol obtained by the demethylation of harmine. An erroneous composition was assigned by Fischer to this substance, which appears to be a molecular compound of norharmolcarboxylic acid (III) with its normal sulphate, and from which the sulphuric acid is readily removed by solution in dilute ammonia and precipitation with acetic acid. The fusion of harmol with potassium hydroxide, therefore, merely oxidises the methyl group to carboxyl. On heating norharmolcarboxylic acid with

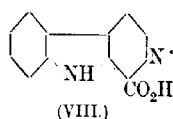
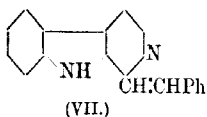
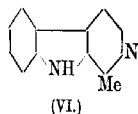
glycerol, the carboxyl group is eliminated and norharmol (IV) is obtained.



his phenolic base is certainly identical with that which was obtained by O. Fischer (*loc. cit.*) by heating harmolic acid, although the specimen was apparently not analytically pure. The nature of norharmol is clearly proved by the fact that on methylation it yields norharmine (V). On distillation with zinc dust in a stream of hydrogen, norharmol is converted into norharman (II).

The second process consists in applying to harman the method whereby harmine was degraded to norharmine (Perkin and Robinson, 1912, 101, 1778).

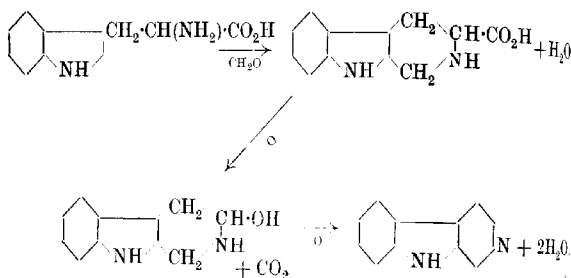
Unfortunately, the paucity of material at our disposal did not permit of an examination of the intermediate stages in the degradation of harman to norharman, but at all stages the substances closely resembled the analogous compounds derived from harmine. Harman (VI) was converted by boiling with benzaldehyde into benzylidenharman (VII), isolated as a sparingly soluble hydrochloride, and this was oxidised by potassium permanganate in pyridine solution with formation of norharmancarboxylic acid (VIII), which yielded norharman (II) on heating with glycerol. Norharman is a beautifully crystalline compound melting at 198° and very similar to harman in its properties.



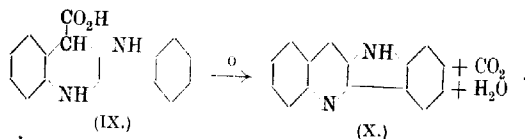
The interest attaching to harman, which was first obtained by O. Fischer (*Chem. Zentr.*, 1901, i, 958) from harmine by the stages harmanol and aminoharman, is much increased by the observation of Späth (*Monatsh.*, 1919, 40, 351) that it is identical with the alkaloid uribine from *Araribra rubra* Mart. and also with loturine from *Symplocosa racemosa* (*Monatsh.*, 1920, 41, 297), whilst coloturine is possibly a crystalline modification. It should also be noted that

Späth confirms the fact, stated in Part IV of this research, that the true melting point of harman is  $238^{\circ}$ , although it is very easy to obtain a lower value.

The relation between harman and tryptophan was discussed in Parts III and IV of this inquiry, and becomes much more significant in view of the fact mentioned above that harman occurs in nature. Our further observations in this connexion will be found in the experimental portion on p. 1616, and it will suffice to point out that harman may be obtained by condensing tryptophan with acetaldehyde in dilute sulphuric acid solution and subsequently oxidising the product with chromic acid. Obviously the replacement of acetaldehyde by formaldehyde in this process should lead to the formation of norharman, and this proved to be the case, and the product was identical with that which had been obtained by the degradation of harmine. The mechanism of these reactions we conceive to be the following, illustrated in the case of the formation of norharman.

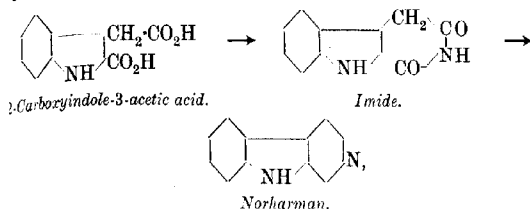


A very similar reaction, in which an oxidation is accompanied by the elimination of a carboxyl group, is to be found in the conversion of dihydroflavindine (IX) into quindoline (X), a change which can be effected with extraordinary facility, and even by shaking an alkaline solution with air at the room temperature (Fichter and Rohner, *Ber.*, 1910, **43**, 3489).

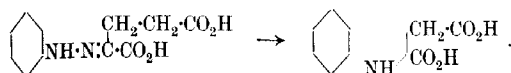


The production of norharman from tryptophan depends on a reaction of a somewhat special type, and as we desired to elaborate more generally applicable methods, attempts were made to build up

the ring system from simple indole derivatives. Our first idea was to attempt the synthesis of norharman by the following stages,

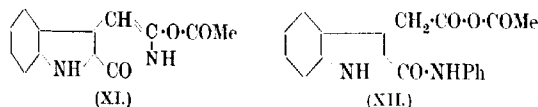


and we accordingly prepared considerable quantities of the 2-carboxyindole-3-acetic acid from  $\alpha$ -ketoglutaric acid and phenylhydrazine by the process of Wislicenus and Waldmüller (*Ber.*, 1911, 44, 1572):



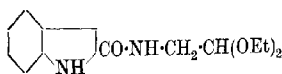
Several well-characterised derivatives of the acid were prepared, such as the dimethyl ester (m. p. 127°), the anhydride (m. p. 250°), and the acid amide (m. p. 244°), but all attempts to obtain the imide either (i) by the action of heat on the amide, (ii) by passing ammonia over the heated anhydride, or (iii) by the action of alcoholic ammonia on the dimethyl ester at elevated temperatures and pressures were unsuccessful. This is remarkable when it is remembered how readily homophthalic acid,  $\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$ , is converted into homophthalimide,  $\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$ , by the action of heat on its ammonium salt.

It is true that the amide of 2-carboxyindole-3-acetic acid on treatment with a mixture of acetic anhydride and acetyl chloride yields a substance,  $\text{C}_{13}\text{H}_{10}\text{O}_3\text{N}_3$ , which appears to be the acetyl derivative of the enimic modification of the imide (XI), but we have not been successful up to the present in attempts to remove the acetyl group and obtain the imide itself. On the other hand, the anilide of 2-carboxyindole-3-acetic acid yields a mixed anhydride with acetic acid (XII) when treated in a similar way.

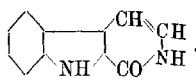


The next series of experiments was based on the hypothesis that

indole-2-carboxyacetalylamide (XIII) might be induced to undergo internal condensation with the formation of the *isocarbo*styryl of the norharman series (XIV), from which norharman could probably be obtained by some process of vigorous reduction.



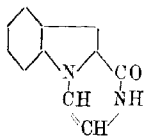
(XIII.)



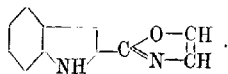
(XIV.)

In connexion with this series of experiments, we first worked out a generally applicable method for the preparation of the chlorides of indole-2-carboxylic acid and allied acids, which consists in allowing the acid to react with phosphorus pentachloride in the presence of acetyl chloride and at the end of the reaction removing the excess of acetyl chloride and phosphoryl chloride by distillation in a high vacuum. The residual chloride is usually sufficiently pure to be directly employed in the preparation of derivatives and the process is convenient.

The chloride of indole-3-carboxylic acid reacts readily with aminoacetal (acetalylamine), and indole-2-carboxyacetalylamide (XIII) is a crystalline substance, melting at  $133^\circ$ , which may be converted by the action of a saturated solution of hydrogen chloride in alcohol at  $40-45^\circ$  into a sparingly soluble, pale yellow, crystalline substance melting at  $247^\circ$ . This compound has the composition  $C_{11}H_8ON_2$ , and is thus derived from the acetalylamide by loss of two molecules of alcohol. It was natural therefore to assume that it was the expected ketodihydronorharman (XIV), but this view was soon found to be untenable, since all attempts to convert the substance into norharman were unsuccessful and a careful study of the reactions of the compound, described in detail on p. 1627, indicated the existence of a free position in the pyrrole nucleus. There appear to be only two other directions in which indole-2-carboxyacetalylamide may lose two molecules of alcohol, and these lead to the expressions XV and XVI for the substance melting at  $247^\circ$ .



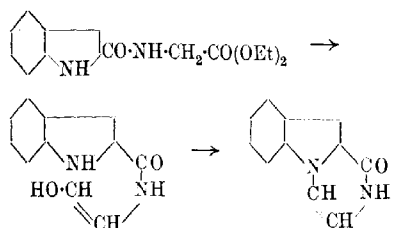
(XV.)



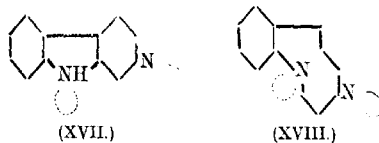
(XVI.)

However, the compound appears to possess a  $-\text{CO}-\text{NH}-$  group capable of enimisation, and its phenolic properties are not in harmony

with the oxazole possibility (XVI), against which may also be urged the melting point and crystalline character of the substance and, much more conclusive, the fact (*vid. infra*) that 1:3-dimethylindole-2-carboxyacetylarnide does not undergo an internal condensation analogous to those described in this communication, although the oxazole possibility remains open. It is clear, therefore, that the formation of the ring during the action of alcoholic hydrogen chloride on indole-2-carboxyacetylarnide has taken place with the help of the hydrogen atom of the  $\text{—NH—}$  group in the indole nucleus according to the scheme

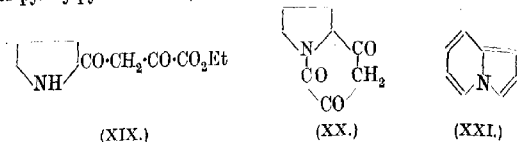


and the substance thus produced has been called 5-keto-4:5-dihydroindole-diazine (1:4) in accordance with a system of nomenclature detailed on p. 1642. Substances of this type do not appear to have been previously prepared, but it is evident that they are readily formed and are very stable. Up to the present oxygenated carbostyryl-like derivatives only have been obtained, but there is no reason why the indole-diazines themselves should be incapable of existence and these bases would probably be found to be of completely aromatic type. That this is possible is seen by a comparison of the cyclic conjugated formulae which can be assigned to 4-carboline (XVII) and indole-diazine (1:4) (XVIII) (compare Perkin and Robinson, T., 1919, 115, 913).

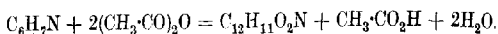


It is proposed to make attempts to produce substances of this type, which clearly have an interest in connexion with the theory of polynuclear aromatic compounds. Quite analogous substances of a similar nature, but containing the pyrrole nitrogen atom only, have already been obtained. Angeli (*Ber.*, 1890, 23, 1793) found

that ethyl pyrrolypyruvate (XIX) underwent ring-closure on treatment with alkaline carbonates with formation of the imine-anhydride of pyrrolypyruvic acid (XX).



The parent substance, an isomeride of indole, was designated pyrindole by Angeli, and this extremely interesting compound has actually been obtained by Scholtz (*Ber.*, 1912, **45**, 734).  $\alpha$ -Picoline is converted by acetic anhydride at 200–220° into a compound,  $C_{12}H_{11}O_2N$ , called picolide and the reaction occurs according to the equation :



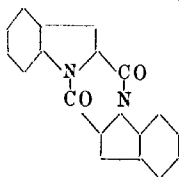
Picolide yields a feeble base,  $C_8H_7N$ , when it is boiled with hydrochloric acid, and this substance was the subject of further investigations (Scholtz, *Ber.*, 1912, **45**, 1718; Scholtz and Fraude, *Ber.*, 1913, **46**, 1069), which resulted in the demonstration that it has the constitution XXI. The feeble basicity of this compound and its resemblance in chemical character to pyrrole and indole are well represented in the cyclic conjugated formulæ XXII and XXIII for pyrrocoline (pyrindole) \* and indole respectively.



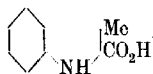
The elucidation of the nature of the substance of melting point 247° renders it very probable that Ciamician and Zatti's anhydride of indole-2-carboxylic acid, obtained by the action of acetic anhydride on the acid (*Ber.*, 1888, **21**, 1932), has the constitution XXIV. This yellow, crystalline substance melts at 312–315°, and whilst

\* The substance  $C_8H_7N$  was at first called "pyrrocoline" and later "pyrindole," in accordance with Angeli's suggestion. The name pyrindole should, however, be reserved for substances containing fused pyridine and pyrrole nuclei (T., 1912, **101**, 1787), and it would avoid the possibility of confusion if Scholtz's compound could retain its original name. The alternative device of renaming the fused pyridine-pyrrole nucleus "pyrindoline" would, unfortunately, lead to the expression "quinindoline" for a fused quinoline-pyrrole nucleus, and this name has already been employed to denote a tetra-nuclear base obtained by Gabriel and Eschenbach (*Ber.*, 1897, **30**, 3020).

affected by aqueous alkalis is hydrolysed by alcoholic potassium hydroxide with formation of potassium indole-2-carboxylate.



(XXIV.)

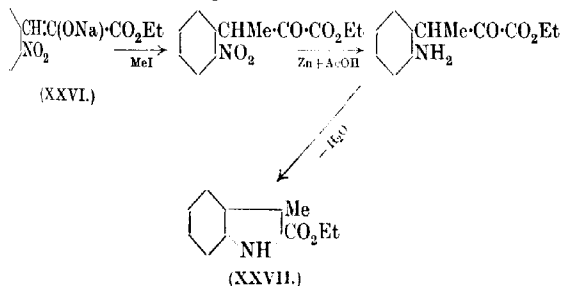


(XXV.)

Further study of the internal condensations of acetylalamides derived from substituted indole-2-carboxylic acids has given results which afford important support to our views on the constitution of the substance melting at  $247^{\circ}$ , and in the first place the behaviour of the acetylalamide of 3-methylindole-2-carboxylic acid (scatole-carboxylic acid) (XXV) was investigated.

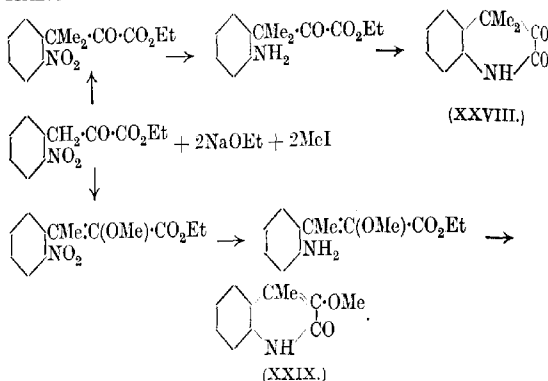
This acid, which was at one time confused with indoleacetic acid, obtained by H. and E. Salkowski (*Ber.*, 1880, **13**, 191, 2217) from the products of the putrefaction of the proteins in animal matter, was synthesised by Arnold (*Annalen*, 1888, **246**, 334) from the enylhydrazone of  $\alpha$ -ketobutyric acid,  $\text{CH}_3\cdot\text{CH}_2\cdot\text{C}(\text{N}_2\text{H}\cdot\text{C}_6\text{H}_5)\cdot\text{CO}_2\text{H}$ , the action of alcoholic sulphuric acid and by Ciamician and Ignanini (*Ber.*, 1888, **21**, 1927) from scatole, sodium, and carbon dioxide. We have found a new method for synthesising the acid which gives good results, and is as follows:

*o*-Nitrotoluene and ethyl oxalate are condensed by means of alcoholic sodium ethoxide in the manner described by Reissert (*Ber.*, 1897, **30**, 1030) to the sodium derivative of ethyl *o*-nitrobenzylpyruvate (XXVI), which is then directly treated with ethyl iodide, and the product on reduction with zinc dust and acetic acid yields ethyl 3-methylindole-2-carboxylate (XXVII), from which the acid is readily obtained by hydrolysis. The process illustrated in the scheme given below:



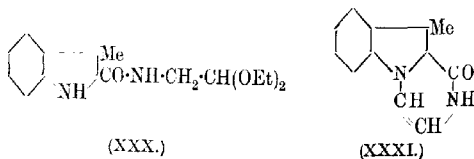


In the course of the series of reactions just described there is also formed in relatively small amount a substance,  $C_{11}H_{11}O_2N$  (m. p.  $217^\circ$ ), which is not an ester and therefore probably owes its existence to the introduction of two methyl groups during the treatment of the sodium derivative of ethyl *o*-nitrophenylpyruvate with methyl iodide. There are two possibilities leading to the formulæ XXVIII and XXIX for this by-product.

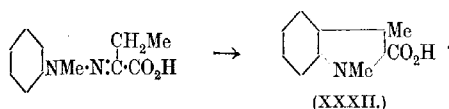


A Zeisel determination proved that the substance,  $C_{11}H_{11}O_2N$ , contains a methoxyl group, and it is therefore clear that the second alternative must be accepted and that the substance is 3-methoxy-4-methyl- $\alpha$ -quinolone.

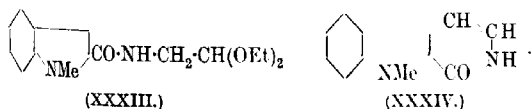
When the chloride of 3-methylindole-2-carboxylic acid is treated with aminoacetal, combination occurs with facility and 3-methylindole-2-carboxyacetalylamide (m. p.  $115^\circ$ ) (XXX) is produced. This substance, on treatment with alcoholic hydrogen chloride, yields a compound,  $C_{12}H_{10}ON_2$ , which melts at  $242^\circ$  and closely resembles the substance of melting point  $247^\circ$  obtained in a similar manner from indole-2-carboxyacetalylamide. In this example it will be noted that ring formation can only occur in the direction already postulated in the case of the substance melting at  $247^\circ$ , and the new compound (m. p.  $242^\circ$ ) must be 5-keto-7-methyl-4:5-dihydroindole-diazine (1:4) (XXXI).



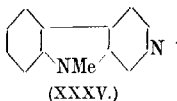
In order to examine the behaviour of a 1:3-disubstituted indole-carboxyacetalyamide, we instituted a series of experiments in which the starting point was 1:3-dimethylindole-2-carboxylic acid (XXXII), readily prepared in the following interesting manner. Ketobutyric acid,  $\text{CH}_3\text{CH}_2\text{CO}\cdot\text{CO}_2\text{H}$  (Wislicenus and Arnold, *Annalen*, 1888, 246, 333), reacts very readily with phenylmethylhydrazine,  $\text{C}_6\text{H}_5\cdot\text{NMe}\cdot\text{NH}_2$ , and it is remarkable that the hydrazone is converted, merely by heating on the steam-bath with dilute hydrochloric acid, almost quantitatively into 1:3-dimethylindole-2-carboxylic acid (m. p.  $213^\circ$ ):



The chloride of this acid also combines with aminoacetal, yielding a crystalline substance,  $\text{C}_{10}\text{H}_{10}\text{N}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}(\text{OEt})_2$ , which melts at  $111^\circ$  and resembles in many ways the other similarly constituted acetalyamides described in this communication. It does not undergo ring formation when treated with alcoholic hydrogen chloride, a behaviour which was to be expected because the two positions essential to ring formation are occupied by methyl groups. The observation is, however, of much interest, as it disposes of the possibility that the substances which we have regarded as indole-diazine derivatives are indyloxazoles (*vid. supra*). From the foregoing it became obvious that the particular synthetic method which depends on ring-closure of an indole-2-carboxyacetalyamide could lead to a derivative of norharman only if the 1-position in the indole nucleus is occupied by a substituent, and we accordingly applied the process to 1-methylindole-2-carboxylic acid, which was prepared by the method of E. Fischer and Hess (*Ber.*, 1884, 17, 61). The chloride of this acid was converted into 1-methylindole-2-carboxyacetalyamide (m. p.  $107^\circ$ ) (XXXIII) in the usual manner, and this substance was fortunately readily converted by alcoholic hydrochloric acid into 2-keto-1-methyl-2:3-dihydro-carboline (m. p.  $242^\circ$ ) (XXXIV). This is a colourless substance, very different in its properties from the indole-diazine derivatives, and resembling norharman more especially in the blue fluorescence which it exhibits in acid solution.



On distillation with zinc dust in a stream of hydrogen, norharman, possibly mixed with its methyl derivative (XXXV), was obtained. The purification of the crude product is described on p. 1638 and was tedious and difficult, but ultimately a pure specimen was obtained and proved to be identical in all respects with norharman obtained as detailed above from harmine and tryptophan.

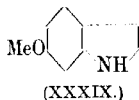
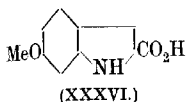
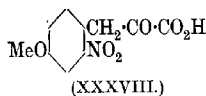
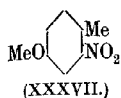


The removal or partial removal of the methyl group at the high temperature of a zinc-dust distillation is not without precedent, and it may be recalled that *N*-methyl-diphenylamine,  $\text{Ph}\cdot\text{NMe}\cdot\text{Ph}$ , yields carbazole and not methylcarbazole by pyrogenic decomposition (Gräbe, *Annalen*, 1874, **174**, 181). The other products of the reaction were hydrogen, nitrogen, methane, benzene, aniline, benzonitrile, and diphenylamine.

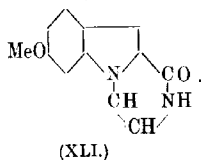
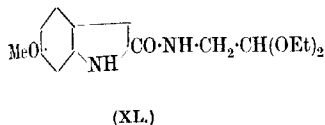
This synthesis of norharman affords direct and independent confirmation of the correctness of the constitution assigned to harmine so far as the nuclear ring system is concerned. Further, the position of the methyl group is placed beyond doubt by a comparison of the reactions whereby norharman and harman are obtained from tryptophan. Synthetical evidence in regard to the position of the methoxyl group is alone lacking, and we are continuing our experiments in this direction, some progress having already been made. In the first place, 6-methoxyindole-2-carboxylic acid (XXXVI) has been synthesised in some quantity by the following series of reactions. *o*-Nitro-*p*-tolyl methyl ether (XXXVII), obtained by the methylation of *o*-nitro-*p*-cresol with methyl sulphate, on treatment with ethyl oxalate in the presence of alcoholic sodium ethoxide, yields *o*-nitro-*p*-methoxyphenylpyruvic acid (XXXVIII).

This interesting new acid is oxidised by hydrogen peroxide with formation of *o*-nitro-*p*-methoxyphenylacetic acid (m. p. 158°), and this is reduced by zinc dust and acetic acid with formation of *o*-azoxy-*p*-methoxyphenylacetic acid,

$\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{NO}\cdot\text{N}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ ,  
(m. p. 174°). On reduction with ferrous hydroxide, *o*-nitro-*p*-methoxyphenylpyruvic acid is converted in good yield into 6-methoxyindole-2-carboxylic acid (m. p. 197°), and this acid loses carbon dioxide on heating with production of 6-methoxyindole (m. p. 92°) (XXXIX), a new member of the little investigated series of the alkyloxyindoles and one of the parent substances of harmine and harmaline.

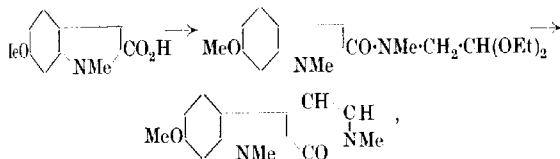


The chloride of 6-methoxyindole-2-carboxylic acid reacts normally with aminoacetal, yielding 6-methoxyindole-2-carboxyacetalylamide (m. p. 123°) (XL), and this on treatment with alcoholic hydrochloric acid is readily converted into 11-methoxy-5-keto-4:5-dihydroindolediazine (1:4) (XLI).

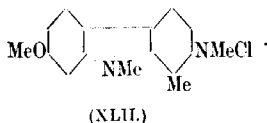


This substance melts at 253° and closely resembles in appearance and properties 5-keto-4:5-dihydroindolediazine (1:4) (XV).

Experiments are in progress which have for their object the preparation of the following series of substances:

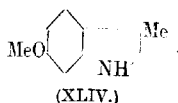
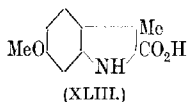


the latter of which is particularly interesting on account of its close relation to harmine and it is hoped that it may be converted into dimethylharmine chloride (XLII) by the action of magnesium methyl iodide followed by treatment with hydrochloric acid.



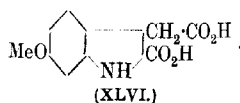
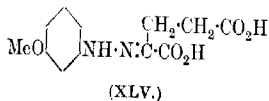
The starting point in this series of reactions will no doubt be most readily obtained from *m*-methoxyphenylmethylhydrazine,  $\text{MeO-C}_6\text{H}_4\text{-NMe-NH}_2$ , by an application of E. Fischer's synthesis

of indole derivatives, and it is therefore of considerable interest that the results incidentally obtained in the course of our experiments go to show that such a synthesis is likely to be successful and that the groups in the benzene nucleus will have the desired orientation. This follows from the identity of the methoxyscatole, which is obtained by the two methods described below. The product of the condensation of *o*-nitro-*p*-tolyl methyl ether and ethyl oxalate in alcoholic sodium ethoxide (*vid. supra*) was directly methylated by means of methyl iodide and subsequently reduced by means of zinc and acetic acid. In this way a good yield of ethyl 6-methoxy-3-methylindole-2-carboxylate (m. p. 128°) is obtained, and from this the 6-methoxy-3-methylindole-2-carboxylic acid (XLIII) is produced by hydrolysis. This methoxyscatolecarboxylic acid melts at 202° with evolution of carbon dioxide and formation of 6-methoxy-3-methylindole (XLIV) or 6-methoxyscatole (m. p. 125°).



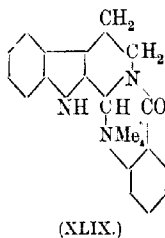
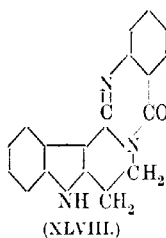
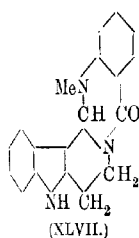
In order to enlarge the basis of synthetical operations in the methoxyindole group, it was considered highly desirable to investigate the behaviour of a suitable *m*-methoxyphenylhydrazine, and it became necessary to devise a method for the preparation of *m*-methoxyphenylhydrazine,  $\text{MeO}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}_2$ , an interesting substance which does not appear to have been described. The base was made in considerable amount from *m*-anisidine by the usual process of diazotisation in hydrochloric acid and reduction with stannous chloride. It distils at 168°/15 mm., solidifying in a freezing mixture, and its stability is remarkable when compared with that of the corresponding *o*- and *p*-derivatives. The methoxyl group in the *ortho*- or *para*-position enormously increases the ease with which the hydrazine is reduced to the related aniline derivative and ammonia, but this effect is evidently unimportant when the methoxyl is in the *meta*-position.

*m*-Methoxyphenylhydrazine condenses readily with  $\alpha$ -keto-glutaric acid, and if the product (XLV) is dissolved in alcohol and the solution saturated with hydrogen chloride, 6-methoxy-2-carboxyindole-3-acetic acid (XLVI) is directly produced.

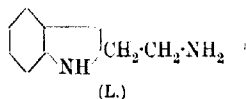


is acid will serve as the basis for a number of experiments which hope to carry out. It melts at 225° and decomposes smoothly with formation of 6-methoxyscatole identical with the substance obtained as described above from *o*-nitro-*p*-tolyl methyl ether by a series of reactions. The important point is thus established that indole-ring formation in the case of a *m*-methoxyphenylhydrazones takes place in the *para*-position with respect to the methoxyl group.

In view of the fact that tryptophan, arbutine (loturine), harmine, and harmaline undoubtedly contain a —C—C—N— chain attached to the 3-position in indole, it would be highly remarkable and surprising if there should exist a series of naturally occurring substances in which a similar chain is attached to the 2-position, although it would, of course, be most unwisely dogmatic to deny the possibility of this. In the case of the alkaloids of *Evodia rutæcarpa*, the brilliant work of Asahina and Mayeda (*J. Pharm. Soc. Japan*, 916, No. 416; consulted only in an abstract, *A.*, 1921, **120**, i, 48) has led to the adoption by these authors of the formulæ XLVII and XLVIII for evodiamine and rutæcarpine respectively, and it will not be out of place to examine the validity of the evidence which rules out the constitutions which would bring these bases into line with the tryptophan group, for example, the expression XLIX for evodiamine.



Evodiamine is hydrolysed, first by alcoholic hydrochloric acid and then by alcoholic potassium hydroxide, with the formation of a base,  $C_{10}H_{12}N_2$ , to which the constitution L is assigned,



and this is the crux of the whole matter. A portion of the evidence, at any rate, is likely to prove fallible, since one of the arguments adduced is to the effect that this base yields indole-2-carboxylic

acid on fusion with potassium hydroxide. Now whilst 2-methyl-indole yields indole-2-carboxylic acid on fusion with potassium hydroxide, it is also true that even such a simple 3-substituted indole as scatole yields some indole-2-carboxylic acid mixed with indole-3-carboxylic acid when submitted to similar treatment (Ciamician and Zatti, *Ber.*, 1888, **21**, 1933). The sole product from the alkali fusion of tetrahydrocarbazole was indole-2-carboxylic acid (Zanetti, *Ber.*, 1893, **26**, 2007). The longer the sidechain of a 3-substituted indole the more numerous will be the opportunities for side-reactions and formation of cyclic structures, and consequently the greater the probability that indole-2-carboxylic acid would result from the vigorous process of fusion with potassium hydroxide. We are inclined to discount the value of this evidence, since the production of indole-2-carboxylic acid would be in harmony with either of the possible views of the nature of the aminoethyl-indole from evodiamine. A much more serious difficulty is found in the fact that the base melts at  $120^{\circ}$  (*N*-benzoyl derivative, m. p.  $173-174^{\circ}$ ), whereas 3- $\beta$ -aminoethylindole, synthesised by Ewins (*T.*, 1911, **99**, 270), melts at  $145-146^{\circ}$  (*N*-benzoyl derivative, m. p.  $137-138^{\circ}$ ). This is apparently conclusive, but there is just the possibility of a loop-hole, such as the existence of the base in polymorphic forms, and the matter is of such interest that it is proposed to attempt an independent synthesis of 3- $\beta$ -aminoethyl-indole, not only with the object indicated above, but also because this base is a very suitable starting point for syntheses in the harmane group.

#### EXPERIMENTAL.

##### *Harman from Tryptophan.*

In Part IV (*T.*, 1919, **115**, 968) of this investigation it was proved that the base,  $C_{12}H_{10}N_2$ , obtained by Hopkins and Cole (*J. Physiol.*, 1903, **29**, 451) by the oxidation of tryptophan with ferric chloride is identical with harman, and the mechanism of the reaction has engaged our attention. A small yield of harman was obtained by following out precisely the directions given by Hopkins, but the result was negative when precautions were taken to exclude alcohol and ether. Professor Hopkins has kindly informed us that in his own experience the results of the oxidation have been variable and yields varying from nothing to more than 30 per cent. of the theory have been obtained, and suggests that the  $C_2$ -group may possibly arise from the ether used to extract the indolealdehyde, which is the second product obtained in the reaction, especially since the oxidation mixture was allowed to remain over-night in

contact with the solvent. Harman may also be obtained from tryptophan by the following processes.

(A) Tryptophan (1 gram) was dissolved in water (250 c.c.) to which sulphuric acid (1 c.c.) and then acetaldehyde (10 c.c. of 20 per cent. aqueous solution) was added. The liquid was boiled during ten minutes, the source of heat removed, and a 10 per cent. aqueous solution of potassium dichromate (50 c.c.) slowly added while the mixture was still hot. After allowing to remain for five minutes, the solution was heated to boiling and then allowed to cool. The excess of oxidising agent was reduced by sulphurous acid and the chromium precipitated by means of sodium carbonate in boiling solution, the faintly alkaline liquid was then filtered and the precipitate washed with boiling water. The combined filtrate and washings were acidified by addition of hydrochloric acid, boiled with animal charcoal, again filtered, and evaporated to a small bulk on the steam-bath. The base was precipitated by the addition of concentrated aqueous sodium hydroxide, collected, washed with water, and dried in a vacuum. The yield was 0.2 gram. After two crystallisations from benzene, the substance was obtained in nearly colourless prisms melting at 237–238°, and at the same temperature when mixed with a specimen of pure harman.

(B) Tryptophan (3 grams) was heated with acetic anhydride (20 c.c.) until dissolved, zinc chloride (2 grams) was then added and the mixture boiled during one minute. Decomposition of the excess of acetic anhydride by the addition of hot water (150 c.c.) led to the separation of a brown oil, which was converted into a yellow, sparingly soluble chromate by aqueous potassium dichromate (60 c.c. of 10 per cent. solution) to which concentrated sulphuric acid (3 c.c.) had been added. The solid was well broken up and the mixture boiled until nearly the whole of the chromate had passed into solution, a stage reached after about twenty minutes. Excess of sodium hydroxide was added and the base extracted by means of ethyl acetate. The ethyl acetate solution was washed with a little water and then with dilute hydrochloric acid. The acid washings were concentrated and on treatment with alkali yielded 0.5 gram of harman, which was crystallised and identified as in the previous example.

(C) Harman was obtained from tryptophan in small yield in various ways, of which the most interesting is the simultaneous oxidation of alanine and tryptophan by means of chromic acid in dilute solution. Tryptophan (1 gram) and alanine (2 grams) dissolved in boiling dilute sulphuric acid (250 c.c.; 0.5 per cent.) were oxidised by the slow addition of potassium dichromate (5



grams) dissolved in water (100 c.c.). The product was worked up as in (A) above and a small yield of harman obtained.

Attempts were made to produce harman by applying to tryptophan a process similar to that which is used for the conversion of diacetonamine oxalate into vinyl diacetonamine oxalate. When tryptophan was boiled with butyl alcohol, oxalic acid, and acetal a brownish-yellow solution exhibiting green fluorescence was obtained. On extraction with dilute sulphuric acid, a solution exhibiting bluish-violet fluorescence was produced, and the reactions of the base which could be obtained from this by treatment of the concentrated liquid with alkali were not those of harman but more nearly resembled those of an alkylated harman. A small amount of *harman butyl iodide* was prepared, and the colour and fluorescence changes in acid, neutral, and alkaline solution were identical with those of the product in the above experiment. A complete examination of the reaction would be of interest, but the amount of tryptophan at our disposal did not permit of this.

#### *Harmolic Acid.*

##### *Norharmolcarboxylic Acid* (Formula III).

The fusion of harmol with potassium hydroxide was carried out exactly as described by O. Fischer (*Ber.*, 1889, **22**, 642) and the isolation of the acid by fractional acidification of the dissolved melt with sulphuric acid was also effected. The crystallised product gave on analysis numbers agreeing closely with those determined by Fischer, namely C = 55.5; H = 3.7; N = 10.8; as against C = 55.6, 55.2; H = 3.8, 3.7; N = 11.1, 11.4 per cent., as given by Fischer. On the basis of these results, Fischer (*loc. cit.*) suggested the formula  $C_{12}H_{10}O_5N_2$ , which is extremely difficult to explain if the constitution of harmine now adopted by the present authors is correct.

In view of the relatively sharp melting point of the product (247°), the problem appeared rather puzzling until the presence of sulphur was established (Found: S = 4.0 per cent.).

The harmolic acid of O. Fischer therefore appears to be a *sulphate of norharmolcarboxylic acid* of the composition  $(C_{12}H_9O_5N_2)_3 \cdot H_2SO_4$  requiring C = 55.2; H = 3.3; N = 10.7; S = 4.1 per cent.

The acid itself is readily obtained by dissolving this curious sulphate in dilute ammonia and precipitating from the filtered hot solution by addition of acetic acid. The very pale yellow powder was well washed with hot water and dried at 140°. It could not be crystallised on account of its extremely sparing solubility in organic solvents, but prepared from pure "harmolic acid" it is practically

homogeneous and melts with much frothing and decomposition at  $272^{\circ}$  after darkening at  $267^{\circ}$  (Found: C = 63.3; H = 3.6; N = 12.6.  $C_{12}H_9O_3N_2$  requires C = 63.1; H = 3.5; N = 12.4 per cent.). The substance is readily soluble in alkalis, and the solutions couple with diazo-salts, forming orange-red azo-derivatives. The compound is also feebly basic, forming yellow salts with mineral acids.

*Norharmol* (Formula IV).

This substance is the phenolic base which O. Fischer obtained by heating harmolic acid (*loc. cit.*), and to which he ascribed the composition  $C_{11}H_{10}ON_2$ . We have obtained the compound by heating pure norharmolecarboxylic acid with glycerol until carbon dioxide was no longer evolved and a clear solution was obtained. On cooling, norharmol separated in nearly colourless needles and was washed with aqueous alcohol and then with alcohol and dried at  $140^{\circ}$  (Found: C = 71.5; H = 4.6; N = 15.2.  $C_{11}H_9ON_2$  requires C = 71.7; H = 4.3; N = 15.2 per cent.).

On heating, the substance sublimes in small needles.

It is soluble in caustic alkalis, but not in sodium carbonate or ammonia, and in alkaline solution it exhibits blue fluorescence and couples with diazo-salts. It is a base dissolving in dilute acids to yellow solutions. The platinichloride was analysed by O. Fischer (*loc. cit.*) and with results agreeing with the composition now suggested.

*Conversion to Norharmine.*—Norharmol (0.5 gram) was heated in a sealed tube at  $150^{\circ}$  with water (25 c.c.), methyl alcohol (10 c.c.), sodium hydroxide (1 gram), and potassium methyl sulphate (3 grams) for three hours. After adding excess of sodium hydroxide, the contents of the tube were extracted with much ether and the ethereal solution was washed with water and dried by potassium hydroxide. After removal of the solvent, a residue was obtained which could be crystallised from benzene in colourless needles melting at  $218^{\circ}$ , alone or mixed with a specimen of pure norharmine (Perkin and Robinson, T., 1912, **101**, 1775).

*Norharman* (4-Carboline) (Formula II).

(4) Norharmol (5 grams) was mixed with zinc dust (100 grams) and carefully distilled in accordance with the usual technique of the operation in a stream of hydrogen, the vapours being passed over a further large amount of zinc dust. The product was converted into the nitrate and this salt crystallised from hot dilute

nitric acid. The base was then precipitated by the addition of sodium hydroxide to an aqueous solution of the purified nitrate, collected, and crystallised from benzene.

(B) Harman (3 grams) was boiled during an hour with pure benzaldehyde (10 c.c.), when the liquid became yellow and water was eliminated. The product was mixed with ether and shaken with hydrochloric acid (10 c.c. of concentrated acid and 15 c.c. of water), when a bright yellow hydrochloride separated. This was collected and washed with ether. The substance is undoubtedly *benzylidenharman hydrochloride*, and is very similar in appearance and properties to the analogous harmine derivative (Perkin and Robinson, *loc. cit.*). When it is treated in alcohol with ammonia, a pale yellow solution is obtained which exhibits a most striking violet fluorescence. The whole of the hydrochloride was dissolved in pure pyridine (20 c.c.) and oxidised by means of a cold saturated solution of potassium permanganate until a pink coloration remaining permanent for an hour was obtained. The excess of permanganate was reduced by warming with a few drops of alcohol and the filtered solution evaporated to a small bulk and mixed with excess of hydrochloric acid. The yellow precipitate was collected and dissolved in the least amount of hot dilute ammonia and acidified with acetic acid. The pale yellow precipitate was collected, washed with hot water, and dried at 100°. It was then heated in a test-tube with a little glycerol until carbon dioxide ceased to be evolved and the glycerol boiled. The product was mixed with water and picric acid added. The bright yellow picrate was collected, washed, and at once decomposed by ammonia in presence of a considerable volume of warm benzene. The separated solution was washed with aqueous sodium hydroxide and dried by solid potassium hydroxide, and after filtration the greater part of the benzene was removed by distillation. The crystals which separated were again crystallised from benzene.

(C) Of the various sets of conditions tested for the conversion of tryptophan into norharman the following gave the most satisfactory results. A mixture of tryptophan (3 grams), water (250 c.c.), sulphuric acid (2 c.c.), and aqueous formaldehyde (5 c.c. of 35 per cent.), added in the order named, was boiled during one minute, the lamp removed, and aqueous potassium dichromate (200 c.c. of 10 per cent.) added and the liquid allowed to cool. Excess of sodium hydroxide was added and the liquid extracted several times with ethyl acetate. The extract was washed with a little dilute sodium hydroxide and then with dilute hydrochloric acid, and it is necessary to do this repeatedly, as norharman hydrochloride is to some extent soluble in ethyl acetate. The combined acid solutions

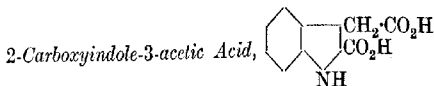
were boiled with animal charcoal, filtered, and evaporated to a small bulk. The base was then precipitated by the addition of excess of sodium hydroxide and collected. The yield was 0.9 gram, which is 36 per cent. of that demanded by theory. The substance is best purified by crystallisation of the nitrate from dilute nitric acid (1:3), this salt being sparingly soluble in the cold and crystallising in slender, yellow needles. The regenerated base is then crystallised from a mixture of ethyl acetate and light petroleum (b. p. 60–70°), and finally from benzene and dried at 100° (Found: C = 78.4; H = 4.8; N = 17.0.  $C_{11}H_8N_2$  requires C = 78.5; H = 4.8; N = 16.7 per cent.).

*Norharman* crystallises from benzene in colourless, slender needles and melts at 198.5°. It is sparingly soluble in cold benzene or light petroleum, moderately soluble in ether or ethyl acetate, and readily soluble in methyl or ethyl alcohol. It is fairly readily soluble in hot water and crystallises on cooling in woolly needles. In neutral solvents, its fluorescence is barely perceptible, but in dilute acid solution it exhibits a vivid blue fluorescence. The specimens of *norharman* prepared according to the methods A and B above melted at 197–198°, and mixed with the especially purified specimen obtained from tryptophan melted at the same temperature. *Norharman* does not exhibit numerous colour reactions. It gives no colour with a pine shaving, nor with *p*-dimethylaminobenzaldehyde and alcoholic hydrochloric acid. Neither does it show any sign of change in presence of vanillin and hydrochloric acid, although the similarly constituted carbazole gives a purple coloration with this reagent. Finally, it does not couple with diazonium salts. On reduction with sodium in boiling butyl-alcoholic solution, a substance is obtained which no longer exhibits fluorescence in acid solution. This product combines to some extent with *p*-nitrobenzenediazonium acetate to a reddish-brown azo-derivative, orange-red on the addition of hydrochloric acid.

The *mercurichloride* crystallises from hot dilute hydrochloric acid in yellow needles and is sparingly soluble.

The *picrate* crystallises from hot water in flocculent, intensely yellow needles melting at 260° with decomposition. It may also be conveniently crystallised from ethyl alcohol in slender needles. It is very sparingly soluble in cold water and alcohol and has frequently been employed as a means of recovering *norharman* from dilute solutions (Found: \* N = 17.8.  $C_{17}H_{11}O_7N_5$  requires N = 17.6 per cent.).

Dried at 100°.



For the purposes of this research, this acid was prepared in quantity by a modification of the process of Wislicenus and Waldmüller (*Ber.*, 1911, **44**, 1572).  $\alpha$ -Ketoglutaric acid (39.3 grams), dissolved in alcohol (300 c.c.), is mixed with a solution of phenylhydrazine (33 grams) in alcohol (200 c.c.) and then a stream of hydrogen chloride passed sufficiently rapidly to raise the alcohol to the boiling point. The liquid first darkens in colour, then becomes less coloured, and ammonium chloride separates. After heating under reflux for an hour, the ammonium chloride is filtered off, washed with alcohol, and the alcoholic hydrogen chloride removed by distillation under reduced pressure.

On the addition of water, the ethyl ester of 2-carboxyindole-3-acetic acid separates as a yellow syrup which soon solidifies and, after recrystallisation from a small quantity of alcohol, melts at  $83-84^\circ$ , as stated by Wislicenus and Waldmüller. In order to obtain the free acid, it is convenient to boil the crude ester with dilute sodium hydroxide (8 per cent.) for about two to three hours. After filtering from a small amount of black tar, the solution is acidified with dilute hydrochloric acid, when, on rubbing, 2-carboxyindole-3-acetic acid separates in small, brown crystals. For analysis, the acid was recrystallised from benzene (Found: C = 60.7; H = 4.5.  $C_{11}H_9O_4N$  requires C = 60.3; H = 4.1 per cent.).

2-Carboxyindole-3-acetic acid melts at  $235-236^\circ$  and exhibits a marked tendency to form supersaturated solutions. It dissolves appreciably in boiling water and separates, on cooling and scratching, in minute white needles; in alcohol, it is readily soluble, but much less so in benzene, and is almost insoluble in light petroleum. The alcoholic solution, mixed with *p*-dimethylaminobenzaldehyde and a drop of hydrochloric acid, becomes reddish-blue on boiling and on cooling the colour largely fades, only a pale blue tint remaining. The deep reddish-blue colour develops again on boiling. The addition of a drop of sodium nitrite changes the cold, pale blue liquid to a deeper blue, which becomes still deeper on boiling. Heated in a test-tube, the acid decomposes with evolution of carbon dioxide, and the residue, boiled with very dilute sodium carbonate, deposits on cooling lustrous plates which melt at  $95^\circ$  and consist of scatole.

*Dimethyl Ester of 2-Carboxyindole-3-acetic Acid,*  
 $C_8H_5N(CO_2Me)(CH_2 \cdot CO_2Me).$

Considerable quantities of this methyl ester were prepared by employing methyl alcohol in the place of ethyl alcohol in the experiment described at the commencement of this section. Most of the methyl alcohol and hydrochloric acid was distilled from the product under reduced pressure, when, on standing, the dimethyl ester separated in green crystals, which were collected and washed with water to remove ammonium chloride. A further yield of less pure material was obtained by diluting the methyl-alcoholic mother-liquor with water, and both crops were purified by recrystallisation from methyl alcohol. The same substance was also obtained by esterifying 2-carboxyindole-3-acetic acid with methyl alcohol and hydrochloric acid in the usual manner (Found : C = 63·2; H = 5·3.  $C_{13}H_{13}O_4N$  requires C = 63·1; H = 5·3 per cent.).

This dimethyl ester melts at 126—127°, is moderately readily soluble in boiling methyl alcohol, and separates in compact prisms. In general it is not so readily soluble in organic solvents as the diethyl ester.

The alcoholic solution, containing *p*-dimethylaminobenzaldehyde and hydrochloric acid, gives on boiling a pale red coloration which becomes more intense on the addition of sodium nitrite.

The anhydride,  $C_8H_5N \begin{smallmatrix} \text{CH}_2 \cdot \text{CO} \\ \diagdown \quad \diagup \\ \text{CO} \end{smallmatrix}$ , is formed when the acid is

heated with acetic anhydride, and the presence of acetyl chloride appears to improve the yield and the purity of the product. A mixture of freshly distilled acetic anhydride (100 grams) and acetyl chloride (10 grams) is added to the acid (20 grams) and the mixture heated gently, at first on the water-bath and then to boiling. The acid dissolves and, when the solution is almost boiling, a mass of crystals separates; after standing for an hour, these are collected, washed with acetic anhydride, and dried at 100°. The yield is about 13 grams, and, for analysis, the anhydride was recrystallised from acetic anhydride (Found : C = 65·4; H = 4·1; N = 6·8.  $C_{11}H_9O_3N$  requires C = 65·7; H = 3·5; N = 7·0 per cent.).

When rapidly heated, this anhydride begins to blacken at 230° and melts with decomposition at about 250°. It is very sparingly soluble in alcohol or ether and insoluble in cold dilute sodium carbonate solution, but it dissolves readily in the latter on boiling.

The Acid-imide,  $C_8H_5N \begin{smallmatrix} \text{CH}_2 \cdot \text{CO}_2\text{H} \\ \diagdown \quad \diagup \\ \text{CO} \cdot \text{NH}_2 \end{smallmatrix}$  (?).—With the object of obtaining the imide, the anhydride was dissolved in naphthalene at 180° and a current of carefully dried ammonia passed, when a

white, sparingly soluble substance separated, which proved to be the amide. Benzene was added to dissolve the naphthalene, and the white powder collected and washed with benzene, when it was found that the substance was readily soluble in dilute sodium carbonate, and analysis proved that it was the amide figured above. The same substance was subsequently more conveniently prepared in the following manner: A mixture of the anhydride (10 grams) with solid ammonium acetate (50 grams) is melted and the melt boiled gently for half an hour. The clear liquid, on cooling and mixing with water and dilute hydrochloric acid, gradually deposits the amide as a green solid, which is purified by crystallisation from alcohol, from which it separates in colourless needles which melt at  $242-244^{\circ}$  with decomposition (Found: C = 60.9; H = 4.6; N = 12.2.  $C_{11}H_{10}O_3N_2$  requires C = 60.6; H = 4.6; N = 12.8 per cent.). The solution of the amide in alcohol containing *p*-dimethylaminobenzaldehyde and hydrochloric acid gives, on boiling, a purple blue coloration which fades somewhat on cooling. The addition of a drop of sodium nitrite in the cold changes the colour, and a peculiar dichroic liquid is obtained which is garnet-red to transmitted and blue to reflected light.

Many experiments were made with this amide in the hope that it might be found possible to convert it into the imide (compare p. 1605). When the amide is heated in a test-tube, decomposition readily sets in and an odour reminiscent of scatole develops, but no imide appears to be formed.

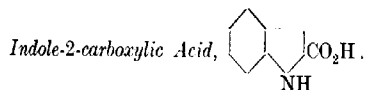
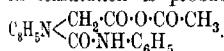
Similarly, the imide was not obtained when the di-ammonium salt of 2-carboxyindole-3-acetic acid was heated. The next attempt to obtain the imide was by heating the amide with acetic anhydride and acetyl chloride. When the amide was gently warmed on the water-bath with acetic anhydride (10 c.c.) and acetyl chloride (2 c.c.), it passed into solution, and, on further heating, the whole soon became semi-solid owing to the separation of a colourless, crystalline substance. After cooling, this was collected and recrystallised from acetic acid, from which it separated in minute, colourless needles which melted, with decomposition, at about  $312^{\circ}$ . This characteristic substance is insoluble in sodium carbonate or hydroxide in the cold, but dissolves in 12 per cent. sodium hydroxide, on gently warming, to a yellowish-green solution (Found: C = 64.3; H = 4.0; N = 11.2.  $C_{13}H_{10}O_3N_2$  requires C = 64.5; H = 4.1; N = 11.6 per cent.). This analysis indicates that the substance is an acetyl derivative of the imide of the probable constitution  $C_8H_5N < \begin{smallmatrix} CH: C \cdot O \cdot CO \cdot CH_3 \\ CO \cdot NH \end{smallmatrix}$ , but so far we have not been successful

in removing the acetyl group and obtaining the imide itself.

Similar want of success attended a series of experiments on the action of ammonia on the dimethyl ester of 2-carboxyindole-3-acetic acid (p. 1623). If the dimethyl ester is heated in a sealed tube with methyl alcohol saturated with ammonia at 0°, no crystalline substance separates, and, on opening the tube, a deep green colour develops on the surface and the liquid stains the skin.

*The Anilide*,  $C_8H_5N < \begin{smallmatrix} CH_2 \cdot CO_2H \\ CO \cdot NH \cdot C_6H_5 \end{smallmatrix}$  (?).—This derivative was prepared by boiling for fifteen minutes a mixture of aniline (5 grams), acetic acid (5 grams), and the anhydride of the acid (2 grams; p. 1623). On mixing the product with dilute hydrochloric acid, a green slime of crystals, containing acetanilide, separated, and these were collected and extracted with dilute ammonia. The alkaline extract was precipitated by hydrochloric acid, and the crystals, which were still sticky, were dissolved in sodium carbonate and again precipitated with hydrochloric acid. The voluminous mass of colourless crystals (2 grams) was collected, washed with water, and recrystallised from alcohol, from which the substance separated in needles melting at 216—217° (Found: C = 69·6; H = 5·0.  $C_{17}H_{14}O_3N_2$  requires C = 69·4; H = 4·8 per cent.). When this anilide (1·6 grams) was warmed with acetic anhydride (10 c.c.) and acetyl chloride (1·5 c.c.), it dissolved, and, on cooling, crystals separated which, after washing with alcohol and crystallising from acetic anhydride, melted at 182° (Found: C = 67·8; H = 4·8; N = 8·2.  $C_{19}H_{16}O_4N_2$  requires C = 67·8; H = 4·8; N = 8·3 per cent.).

This substance is insoluble in dilute sodium carbonate or hydroxide and evidently corresponds with the mixed anhydride of the anilide of 2-carboxyindole-3-acetic acid and acetic acid. Its constitution is probably that represented by the formula



This acid, which we required in considerable quantities, was, in the first instance, prepared from pyruvic acid and phenylhydrazine by the method discovered by E. Fischer (*Annalen*, 1866, **236**, 142). Subsequently, a modification of the process described by Reissert (*Ber.*, 1897, **30**, 1030) was worked out, which was found to be convenient, and is briefly as follows:—*o*-Nitrophenylpyruvic acid,  $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot CO \cdot CO_2H$  (20·9 grams), prepared as described by



Reissert, is dissolved in ammonia (140 c.c. of *d* 0.880 diluted with 200 c.c. of water), a hot solution of crystallised ferrous sulphate (180 grams in 200 c.c. of water) gradually added, and the whole first warmed on the water-bath for half an hour and then boiled for the same time. After filtering, the filtrate and washings of the ferric oxide are concentrated considerably and acidified, when indole-2-carboxylic acid separates in the form of a white, crystalline powder, which, after remaining over-night, is collected, washed with cold water, and dried in the steam-oven. In this condition the acid is nearly pure, melts at  $202-204^{\circ}$ , and the yield is 12-13 grams, or about 70 per cent. of theory.

On heating in alcoholic solution with *p*-dimethylaminobenzaldehyde and hydrochloric acid, indole-2-carboxylic acid develops a red coloration, which fades on cooling and returns again on boiling.

*Indole-2-carboxyacetylamide* (Formula XIII).

As stated in the introduction, this substance is produced when aminoacetal reacts with indole-2-carboxylic chloride. The preparation of this acid chloride was found to be a matter of some difficulty, but ultimately the following procedure led to the desired result.

Indole-2-carboxylic acid (3.2 grams), thoroughly dried, powdered, and passed through a fine sieve, is placed in a small fractionating flask, mixed with freshly distilled acetyl chloride (35 grams), and then powdered phosphorus pentachloride (4.2 grams) gradually added to the suspension, the whole being well cooled during the addition. The flask is removed from the ice and gently warmed by the heat of the hand until the pentachloride has disappeared. After remaining at the ordinary temperature for four hours, the flask is connected with the pump, and the acetyl chloride and phosphoryl chloride are removed by warming in water at about  $40^{\circ}$ , and finally at  $50-55^{\circ}$ . The residual acid chloride, although somewhat brown, is pure enough for the next operation, which is carried out as follows. The acid chloride is dissolved in warm dry chloroform (30 c.c. distilled over phosphoric oxide), the solution filtered rapidly from a little brownish-red impurity, cooled, and then aminoacetal (5.4 grams) dissolved in dry chloroform (10 c.c.) added, the vigorous reaction being controlled by careful cooling. After fifteen minutes, the flask is removed from the ice and salt, the chloroform distilled off under reduced pressure, the residue mixed with water, the crystalline precipitate collected with the aid of the pump, and dried on porous porcelain in a vacuum desiccator. The yield is about 80 per cent. of theory, and the substance, in this

condition, melts at 131–132° and is almost pure. For analysis it was crystallised from alcohol (Found: C = 65.5; H = 7.3; N = 10.4.  $C_{12}H_{10}O_3N_2$  requires C = 65.2; H = 7.2; N = 10.2 per cent.).

*Indole-2-carboxyacetalylamide* melts at 133°, is readily soluble in alcohol, but less so in benzene, and crystallises from either solvent in small, colourless needles. It is very readily soluble in ether, but sparingly so in light petroleum. It decomposes gradually at 90°, turning yellow and giving off alcohol, and this decomposition takes place rapidly at about 140°. In a quantitative experiment carried out under these conditions, it was found that the acetalist 26.7 per cent. of alcohol, whereas the elimination of one molecule of alcohol corresponds with 16.7 and that of two molecules with 33.3 per cent. loss. The residue is a hard, brittle mass sparingly soluble in most neutral organic solvents. It dissolves in hot acetic acid, but does not separate on cooling, and the addition of water precipitates an amorphous powder, which was not further investigated.

*5-Keto-4:5-dihydroindolediazine (1:4) (Formula XV).*

When indole-2-carboxyacetalylamide (2 grams) is added to a saturated solution of hydrogen chloride in alcohol at 40–45°, it soon dissolves to a deep yellowish-brown solution, and in a few minutes yellow crystals separate. After half an hour, the crystals are collected with the aid of the pump and recrystallised from boiling alcohol, in which the substance is sparingly soluble and from which it separates in short, yellow needles melting at 247° (Found: C = 72.2; H = 4.7; N = 14.9.  $C_{11}H_8ON_2$  requires C = 71.7; H = 4.3; N = 15.2 per cent.). The bright yellow solution of this compound in ethyl alcohol fluoresces green, but the addition of a drop of concentrated aqueous potassium hydroxide produces a duller yellow liquid which exhibits bluish-violet fluorescence, and the reaction is evidence of the phenolic (enimic) character of this cyclic amide. That it contains a free position in the pyrrole nucleus is very probable in view of the following observations. A pine shaving is coloured a weak mauve-red by a hot alcoholic hydrochloric acid solution of the substance. When an alcoholic solution is heated with an equal volume of concentrated hydrochloric acid and a trace of *p*-dimethylaminobenzaldehyde added, a green coloration which becomes blue on the addition of water is obtained. The addition of vanillin to a suspension of the compound in concentrated hydrochloric acid causes a reddish-purple coloration even in the cold. On warming, this becomes very intense, and on the addition of water a purple precipitate is thrown

down. Addition of sodium hydroxide causes a colour change through blue and green to yellow. *p*-Nitrobenzenediazonium chloride to which sodium acetate in excess is added gives with an alcoholic solution of the substance a yellow colour changing to orange and reddish-brown and finally a reddish-brown precipitate of an azo-derivative. In presence of sodium hydroxide, the coupling occurs immediately to a deep bordeaux-red solution, and the reddish-brown precipitate is obtained on acidification. On boiling the substance (m. p. 247°) with concentrated hydrochloric acid, the initially clear yellow solution clouds at a certain stage and becomes faintly green. The crystalline material in suspension becomes viscous, and on the addition of water a sulphur-yellow material is precipitated. The reaction suggests polymerisation and instability to vigorous treatment with acids. No doubt the very unusual constitution of this compound would modify the indole colour reactions to a considerable extent, and tests were therefore also applied to a reduction product which can be obtained by the action of an excess of sodium in boiling butyl alcohol. The pine-shaving reaction was mauve-red, and stronger than with the original substance. The dimethylaminobenzaldehyde reaction was rose-red, the vanillin-hydrochloric acid reaction was bright red, changing to purple on heating, whilst the coupling with *p*-nitrobenzenediazonium acetate gave a brownish-red as before, but the azo-derivative was in this case an indicator, and changed to crimson on the addition of hydrochloric acid. At an early stage of this investigation, it was thought that this substance might be a derivative of 4-carboline, and attempts were made in various directions to convert it into norharman, but uniformly without success. The products of distillation with zinc dust are indole and an orange base which sublimes readily and dissolves in dilute acids to an intense orange-yellow solution. This interesting substance could not be obtained in sufficient amount for examination. It may also be mentioned that the action of magnesium methyl iodide on the compound (m. p. 247°) in benzene solution results in the production of a base which fluoresces violet in ethyl acetate solution, but does not exhibit fluorescence in aqueous acid solution, a behaviour which is the reverse of that of harman.

*Condensation of Indole-2-carboxylic Chloride with Alanine Ester  
and with the Sodium Derivative of Ethyl Acetoacetate.*

*Indole-2-carboxy- $\alpha$ -(carbethoxy)ethylamide,*  

$$\text{C}_8\text{H}_6\text{N}\cdot\text{CO}\cdot\text{NH}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}.$$

—This substance was readily obtained by the mixing of the acid

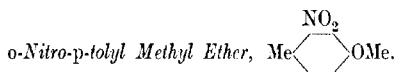
chloride from 1.6 grams of indole-2-carboxylic acid (p. 1626) with a chloroform solution of alanine ester (2.4 grams), when a colourless, crystalline substance soon separated. This (1.4 grams) was collected, washed with chloroform, and dried in a vacuum desiccator over sulphuric acid, when it melted at  $202^{\circ}$  (Found: C = 64.4; H = 6.2.  $C_{14}H_{16}O_3N_2$  requires C = 64.6; H = 6.2 per cent.).

$\beta$ -Carbethoxy- $\alpha$ -methylvinyl Indole-2-carboxylate,



—The interaction of indole-2-carboxylic chloride with the sodium derivative of ethyl acetoacetate was studied in the hope that the product, on hydrolysis, might yield 2-acetylindole,  $C_8H_6N\cdot CO\cdot CH_3$ , but apparently it is formed by the interaction of the acid chloride with the enol modification of ethyl acetoacetate. Indole-2-carboxylic acid (3.2 grams) was converted into the acid chloride in the usual manner (p. 1626), and the latter, dissolved in ether, added to an alcoholic solution of the sodium derivative of ethyl acetoacetate prepared from sodium (1 gram) and ethyl acetoacetate (5.2 grams). As there was little apparent change after twenty-four hours, the ether was slowly distilled off and the alcoholic solution heated on the steam-bath for half an hour. On adding water, a rather dark, semi-solid mass separated, which was collected, washed, and crystallised first from alcohol and then from benzene (Found: C = 66.0; H = 5.3.  $C_{15}H_{15}O_4N$  requires C = 65.9; H = 5.5 per cent.).

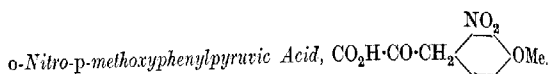
This substance melts at  $101^{\circ}$ , is insoluble in dilute sodium hydroxide, and gives, in alcoholic solution with ferric chloride, only a faint green coloration. It therefore appears likely that it has the constitution assigned to it above.



This substance may be readily obtained from  $o$ -nitro- $p$ -tolyl carbonate (Friedländer, "Fortschritte der Theerfarben Fabrikation," Vol. 9, p. 151) by hydrolysing with excess of sodium hydroxide solution and adding to the well-cooled product methyl sulphate and sufficient sodium hydroxide.

A better plan is to precipitate the  $o$ -nitro- $p$ -cresol from the alkaline solution, obtained by the hydrolysis of the carbonate, by hydrochloric acid, to collect this with the aid of the pump, dry on porous porcelain and then methylate in the following way. Sodium (2 mols.), dissolved in the minimum quantity of methyl alcohol, is added to the solution of  $o$ -nitro- $p$ -cresol (1 mol.) in methyl alcohol, the whole well cooled, and then methyl sulphate (1 mol.) added slowly with shaking and cooling. The product is warmed on the

water-bath for half an hour, cooled, the sodium sulphate filtered off, and washed with a little methyl alcohol. The methyl alcohol is distilled off under reduced pressure, water added, and the crude methyl ether extracted with benzene and then the benzene solution extracted with dilute sodium hydroxide. After drying over calcium chloride and distilling off the benzene, the *o*-nitro-*p*-tolyl methyl ether is distilled under reduced pressure; it boils constantly at 150°/20 mm. The yield approximates to the theoretical.

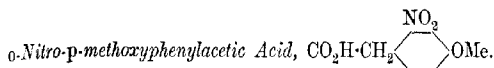


In preparing this acid, sodium (9.2 grams), dissolved in alcohol (92 grams), was cooled and gradually mixed with ethyl oxalate (29.2 grams). *o*-Nitro-*p*-tolyl methyl ether (16.6 grams) was then added and the mixture kept at 35–40° in a thermostat for three days. The dark reddish-brown, gelatinous mass was cooled in ice, decomposed by the calculated amount of a mixture of equal weights of concentrated hydrochloric acid and ice and most of the alcohol distilled off from the water-bath under reduced pressure. The salt which had separated was removed with the aid of the pump, washed with ether, and the liquid extracted with ether until the extract was scarcely coloured red by the addition of sodium hydroxide. The ethereal solution was repeatedly shaken with dilute sodium hydroxide (5 per cent.), when, on acidifying the alkaline extract, crude *o*-nitro-*p*-methoxyphenylpyruvic acid separated and was extracted with ether. On standing, the ethereal solution deposited a small quantity of a substance very sparingly soluble in ether; this was removed by filtration and the ethereal solution dried and concentrated.

On adding benzene, the new acid gradually separated in a crystalline condition and was recrystallised from benzene, from which it separated in well-developed, yellow needles. These crystals contain benzene of crystallisation, melt at about 80°, but when heated rather below this temperature they become opaque and the melting point is then 144–145°. The loss in weight was found to be only 7.5 per cent., corresponding with the formula  $4\text{C}_{10}\text{H}_9\text{O}_6\text{N}\cdot\text{C}_6\text{H}_6$ , which contains 7.5 per cent. of benzene (Found: in material heated at 80–90° until the weight was constant, C = 50.3; H = 3.9; N = 5.8.  $\text{C}_{10}\text{H}_9\text{O}_6\text{N}$  requires C = 50.2; H = 3.8; N = 5.8 per cent.).

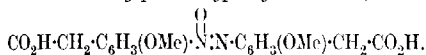
*o*-Nitro-*p*-methoxyphenylpyruvic acid is readily soluble in ether, alcohol, or acetic acid, but sparingly so in benzene. It dissolves

appreciably in boiling water, and separates, on cooling, in pale greenish-yellow needles. Sodium hydroxide dissolves it with a deep purplish-red coloration. It reacts with phenylhydrazine, yielding a substance which melts at about  $157^{\circ}$ , but this has not been further investigated.



This acid is readily obtained under the following conditions: *o*-Nitro-*p*-methoxyphenylpyruvic acid, dissolved in the minimum amount of sodium hydroxide (2 per cent.), is cooled in ice-water and hydrogen peroxide solution slowly added until a test portion gives only a faint red coloration with sodium hydroxide. On acidifying, *o*-nitro-*p*-methoxyphenylacetic acid is precipitated as a sandy powder and may be recrystallised from 50 per cent. acetic acid, from which it separates in yellow needles. It melts at  $157-158^{\circ}$  and decomposes vigorously when it is heated, a fact which rendered analysis difficult (Found: N = 7.1.  $\text{C}_8\text{H}_7\text{O}_5\text{N}$  requires N = 6.7 per cent.).

*o*-Azoxy-*p*-methoxyphenylacetic Acid,



Reissert (*Ber.*, 1909, **41**, 3924), in describing his experiments on the reduction of *o*-nitrophenylacetic acid to dioxindole with zinc dust and sulphuric acid, mentions that he obtained as by-product, azoxyphenylacetic acid. On reducing *o*-nitro-*p*-methoxyphenylacetic acid under the same conditions, the main product isolated was the azoxy-derivative. *o*-Nitro-*p*-methoxyphenylpyruvic acid (1.7 grams) was oxidised with hydrogen peroxide to *o*-nitro-*p*-methoxyphenylacetic acid under the conditions given in the last section, and the latter acid was precipitated by adding sulphuric acid (10 c.c. of 50 per cent.). Zinc dust (1.3 grams of 90 per cent.) was then added in small quantities and with vigorous shaking, the temperature being kept at about  $30^{\circ}$ . After remaining over-night, the solid was collected, washed well, and recrystallised from 50 per cent. acetic acid, from which the azoxy-derivative separated in almost, brownish-yellow needles which melted at  $173-174^{\circ}$  (Found: C = 58.0; H = 5.1; N = 8.0.  $\text{C}_{18}\text{H}_{18}\text{O}_7\text{N}_2$  requires C = 57.7; H = 4.8; N = 7.5 per cent.).

*6-Methoxyindole-2-carboxylic Acid* (Formula XXXVI).

This acid is obtained from *o*-nitro-*p*-methoxyphenylpyruvic acid by reduction with ferrous sulphate and ammonia under the conditions already described in detail in the case of the preparation of indole-2-carboxylic acid from *o*-nitrophenylpyruvic acid (p. 1625). The only point of difference is that the ammonium salt of the methoxy-acid is less soluble than that of the unsubstituted acid, and usually crystallises out to some extent from the filtrate of the ferric oxide sludge, which requires therefore to be well washed with hot water. On acidifying the ammoniacal filtrate, 6-methoxyindole-2-carboxylic acid separates as a sandy, crystalline powder, the yield being about 70 per cent. calculated on the pyruvic acid employed (Found: C = 63.0; H = 4.7.  $C_{10}H_9O_3N$  requires C = 62.8; H = 4.7 per cent.).

*6-Methoxyindole-2-carboxylic acid* closely resembles indole-2-carboxylic acid in appearance and in many of its properties. It melts at 196–197°, and decomposes a few degrees above this into carbon dioxide and 6-methoxyindole (see below). It is readily soluble in boiling alcohol, and, when the solution is allowed to cool slowly, the acid separates in well-defined, prismatic needles. It crystallises from acetic acid in lustrous plates which lose their lustre on heating in the water-oven owing to elimination of acetic acid of crystallisation. The boiling solution in alcoholic hydrochloric acid gives with *p*-dimethylaminobenzaldehyde, a red coloration, which almost disappears on cooling; the addition of sodium nitrite then produces a deep greenish-blue coloration.

*6-Methoxyindole* (Formula XXXIX).

This new derivative of indole is obtained when 6-methoxyindole-2-carboxylic acid is cautiously heated in a test-tube by means of a sulphuric acid bath somewhat above its melting point (197°) until decomposition is complete. The residue is boiled with water containing a little sodium carbonate and filtered hot, when, on cooling, 6-methoxyindole separates in colourless, glistening leaflets (Found: C = 73.2; H = 6.2.  $C_9H_9ON$  requires C = 73.4; H = 6.1 per cent.).

*6-Methoxyindole* melts at 91–92° and has a faint and not unpleasant odour somewhat reminiscent of that of indole, with which substance it exhibits considerable similarity in appearance and properties.

It is readily soluble in the usual organic solvents with the exception of light petroleum, from which it can very conveniently

be recrystallised. When heated in alcoholic solution with *p*-dimethylaminobenzaldehyde and a drop of hydrochloric acid, a purplish-red colour develops, which does not fade on cooling. The addition of a drop of sodium nitrite intensifies the colour. If, however, the alcoholic solution is mixed with several drops of hydrochloric acid and heated, the initially red solution becomes more deeply coloured, then bluer, and ultimately a somewhat faint greenish-blue, and the colour is intensified by adding nitrite.

6-Methoxyindole-2-carboxyacetyl-*amide* (Formula XL).

This substance is obtained by the action of aminoacetal on the chloride of 6-methoxyindole-2-carboxylic acid essentially under the conditions described in detail in the case of the preparation of indole-2-carboxyacetyl-*amide* (p. 1626). The principal difference noticed was that the methoxy-acid appeared to react more readily and smoothly with phosphorus pentachloride than the unsubstituted acid (Found: C = 62.9; H = 7.2.  $C_{16}H_{22}O_4N_2$  requires = 62.7; H = 7.2 per cent.).

This acetyl-*amide* is very similar in appearance and properties to indole-2-carboxyacetyl-*amide*, and is also decomposed on heating with elimination of alcohol and formation of a resinous substance.

It melts at 123° and crystallises well from benzene, in which solvent, as also in alcohol, it is more readily soluble than the simpler compound.

11-Methoxy-5-keto-4 : 5-dihydroindole-2-diazine (1 : 4) (Formula XLI).

In preparing this substance, 6-methoxyindole-2-carboxyacetyl-*amide* is added to a saturated solution of hydrogen chloride in alcohol and kept at 40–45° until yellow crystals separate. After remaining over-night, the precipitate is collected and recrystallised from alcohol (Found: C = 67.1; H = 4.8.  $C_{13}H_{10}O_2N_2$  requires C = 67.3; H = 4.7 per cent.).

Methoxyketodihydroindole-2-diazine melts at 253° with previous sintering. It is moderately soluble in acetone, less soluble in alcohol, and still less so in benzene, and separates from alcohol in well-defined, yellow needles. Both this substance and ketodihydroindole-2-diazine (m. p. 247°; p. 1627) exhibit a vivid blue fluorescence in neutral or alkaline, but not in acid, solution, and this effect is best seen with the aid of the light of burning magnesium ribbon.



*3-Methylindole-2-carboxylic Acid (Scatole-2-carboxylic Acid)*  
(Formula XXV).

It is stated in the introduction (p. 1609) that this acid may be conveniently prepared from the product of the condensation of *o*-nitrotoluene with ethyl oxalate and sodium ethoxide, by direct methylation followed by the reduction of the product. The condensation product prepared as recommended by Reissert (*Ber.*, 1897, **30**, 1030), after keeping at 40° for three days, is cooled and the red, gelatinous mass mixed with one and a half times the calculated quantity of methyl iodide, when decomposition sets in at once with some evolution of heat. The mixture is heated to boiling for two days, during which the red colour changes to brown, the alcohol and excess of methyl iodide are then distilled off under reduced pressure, water is added, and the whole extracted three times with ether. After washing well with water and drying over calcium chloride, the ethereal solution is allowed to remain over-night, during which it deposits a small quantity of a reddish-brown, crystalline substance, which was not further examined. The filtered ethereal solution is evaporated and the yellowish-brown syrup—which presumably consists mainly of *ethyl α-keto-β-o-nitro-phenylbutyrate*,  $C_8H_7(NO_2) \cdot CHMe \cdot CO \cdot CO_2Et$ —(5 grams) is dissolved in glacial acetic acid (30 c.c.) and gradually reduced by zinc dust (13 grams of 90 per cent.), the addition of the latter being so regulated that the temperature does not rise above 50°. The product is mixed with water, extracted several times with ether, the ethereal solution, which exhibits a striking bluish-green fluorescence, washed with water and dilute sodium carbonate solution, and quickly dried over potassium carbonate, during which *3-methoxy-4-methyl-α-quinolone* commences to separate (see below). The ethereal solution is rapidly filtered and left for two days in the ice chest, filtered from the quinolone and evaporated, when a yellow syrup remains which gradually crystallises and ultimately becomes semi-solid. Purification is best achieved by distilling the whole under reduced pressure, when the ethyl ester passes over at 210°/8 mm., leaving a considerable carbonaceous residue. The ester soon solidifies, and may be crystallised from alcohol, from which it separates in stout needles melting at 135° (compare Wislicenus and Arnold, *Annalen*, 1888, **246**, 334) (Found : C = 70·7; H = 6·4.  $C_{12}H_{13}O_2N$  requires C = 70·9; H = 6·4 per cent.).

*3-Methylindole-2-carboxylic acid* is readily obtained from the ester by boiling with methyl-alcoholic potassium hydroxide, adding water, evaporating off the methyl alcohol, and acidifying with hydrochloric acid, when the acid separates as a putty-like mass,

which soon solidifies and crystallises well from dilute acetic acid in needles melting at  $164^{\circ}$  (Found: C = 68.5; H = 5.2.  $C_{10}H_9O_2N$  requires C = 68.6; H = 5.1 per cent.).

3-Methoxy-4-methyl- $\alpha$ -quinolone,  $C_6H_4 \begin{smallmatrix} \text{CMe} \cdot \text{C} \cdot \text{OMe} \\ | \\ \text{NH} \cdot \text{CO} \end{smallmatrix}$  (cf. p. 1610).

This substance, obtained as described above, is produced only in a yield of about 2 per cent. under these conditions. It melts at  $217^{\circ}$ , is almost insoluble in ether, and sparingly so in alcohol, from which it separates in concentric groups of needles (Found: C = 70.0; H = 5.6; N = 7.4; MeO = 16.9.  $C_{11}H_{11}O_2N$  requires C = 69.8; H = 5.8; N = 7.4; MeO = 16.4 per cent.). Methoxymethylquinolone is insoluble in warm dilute ammonia, but dissolves immediately in methyl-alcoholic potassium hydroxide (25 per cent.) in the cold, and a crystalline substance is deposited, which is apparently a potassium derivative. On acidifying with hydrochloric acid, the quinolone separates as a chalky mass consisting of microscopic, fern-like leaves.

### 3-Methylindole-2-carboxyacetalylamide (Formula XXX).

In preparing this substance, 3-methylindole-2-carboxylic acid (1.7 grams) was suspended in freshly distilled acetyl chloride (20 grams) and gradually mixed with phosphorus pentachloride (2.1 grams), rise of temperature being avoided. The product was treated exactly as described in the case of the chloride of indole-2-carboxylic acid (p. 1626) and very carefully mixed with a dry chloroform solution of aminoacetal (3 grams), and it is necessary in this case to take special care to avoid rise of temperature, otherwise a dark product is obtained.

After distilling off the chloroform under reduced pressure, the residue is recrystallised from benzene. The yield is more than 40 per cent. of theory (Found: C = 66.4; H = 7.7.  $C_{16}H_{22}O_3N_2$  requires C = 66.2; H = 7.6 per cent.).

3-Methylindole-2-carboxyacetalylamide separates from benzene, in which it is moderately readily soluble, in colourless needles and melts at  $115^{\circ}$ .

### 5-Keto-7-methyl-4:5-dihydroindole-diazine (1:4) (Formula XXXI).

This substance is obtained when 3-methylindole-2-carboxyacetalylamide is mixed with alcoholic hydrogen chloride and the mixture warmed to  $40\text{--}45^{\circ}$  (compare p. 1627). Yellow crystals

separate, which are collected and twice recrystallised from alcohol (Found: C = 72.9; H = 5.0.  $C_{12}H_{10}ON_2$  requires C = 72.7; H = 5.0 per cent.).

This substance melts at  $210^\circ$  and in appearance and properties closely resembles 5-keto-4:5-dihydroindole-diazine (p. 1627). Both substances dissolve in alcohol, yielding pale yellow solutions which fluoresce green. When sodium is added to the solution of either in boiling butyl alcohol, reduction takes place and the solutions exhibit a remarkable yellowish-green fluorescence. Again, both substances couple readily with diazotised sulphanilic acid, yielding dyes which dissolve in alkalis with an orange-yellow and in acids with a yellow colour and dye wool yellow from an acid bath. The relation of these substances to 1-methylisoquinoline is a close one both in regard to formal constitution and properties.

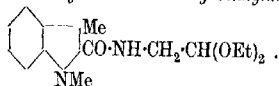
### 1:3-Dimethylindole-2-carboxylic Acid (Formula XXXII).

This acid, which does not appear to have been previously described, is obtained from  $\alpha$ -ketobutyric acid by simply heating with *as*-phenylmethylhydrazine and hydrochloric acid on the steam-bath. Methyloxalacetic ester (Wislicenus and Arnold, *Annalen*, 1888, 246, 336; 12 grams) is added to a mixture of concentrated hydrochloric acid (30 c.c.) and water (60 c.c.) and the whole gently boiled until the evolution of carbon dioxide has ceased and the oil has completely disappeared. After allowing to cool, crude phenylmethylhydrazine\* (10 grams) is added and the mixture heated on the steam-bath, when, in a short time, needles of dimethylindole-carboxylic acid commence to separate and soon fill the liquid. The acid, after being collected, washed, and dried at  $100^\circ$ , melts at  $197-200^\circ$  and the yield is almost theoretical. In this condition it may be used directly for the work described below. For analysis, it was recrystallised from benzene containing a little alcohol (Found: C = 70.0; H = 6.0; N = 7.6.  $C_{11}H_{11}O_2N$  requires C = 69.9; H = 5.8; N = 7.4 per cent.).

1:3-Dimethylindole-2-carboxylic acid decomposes suddenly at about  $213^\circ$  without previous fusion. It is readily soluble in alcohol, but almost insoluble in cold benzene or light petroleum, and separates from a mixture of benzene and alcohol as a colourless crystalline powder. The alcoholic solution, mixed with *p*-dimethylaminobenzaldehyde and hydrochloric acid, gives no coloration until nitrite is added and then a red colour develops, which slowly fades.

\* For such purposes, the crude mixture of phenylmethylhydrazine with some methylaniline which results from the reduction of nitrosomethylaniline with zinc dust and acetic acid may be generally used with success.

## 1 : 3-Dimethylindole-2-carboxyacetalylamide,



In preparing this substance, 1 : 3-dimethylindole-2-carboxylic acid is first made into the acid chloride with acetyl chloride and phosphorus pentachloride in the usual manner (p. 1626), and this is then condensed with aminoacetal in chloroform solution. After distilling off the chloroform and adding water, the crystalline mass is collected, dried on porous porcelain, and crystallised from a mixture of benzene and light petroleum (Found: C = 67.1; H = 7.9.  $\text{C}_{17}\text{H}_{24}\text{O}_3\text{N}_2$  requires C = 67.2; H = 7.9 per cent.).

This substance separates from a mixture of benzene and light petroleum in long, colourless hairs and melts at 110–111°. In its properties, and especially in its manner of crystallising from various solvents, it differs rather markedly from the other substituted aminoacetals described in this communication. Although there was no probability of a diazine being formed, some of the substance was treated in the usual manner with alcoholic hydrogen chloride (p. 1627), but no darkening of the solution took place, nor did crystals separate. On adding water, a sticky substance was deposited, which may have been the corresponding aldehyde, or an oxazole derivative, but the matter was not further investigated.

## 1-Methylindole-2-carboxyacetalylamide (Formula XXXIII).

The 1-methylindole-2-carboxylic acid required for the preparation of the above substance was obtained from phenylmethylhydrazine and pyruvic acid by the method described by E. Fischer and O. Hess (*Ber.*, 1884, **17**, 561). This acid gives, in alcoholic solution, with *p*-dimethylaminobenzaldehyde and hydrochloric acid, a deep purple coloration which fades somewhat on cooling. A drop of sodium nitrite then gives a more intense red, which fades on boiling.

The acid chloride was made by acting on the acid (3.5 grams) with acetyl chloride (30 c.c.) and phosphorus pentachloride (4.2 grams) in the usual manner (p. 1626). The conversion of the chloride into 1-methylindolyl-2-aminoacetal also proceeds normally (p. 1626), but the product, after distilling off the chloroform, exhibited little tendency to crystallise until it was rubbed with water. The crude crystalline mass, after being collected and dried, weighed 4.6 grams and was nearly pure (m. p. 102–103°). For analysis, it was recrystallised from benzene and then melted at

106–107° (Found: C = 66.4; H = 7.6.  $C_{16}H_{22}O_3N_2$  requires C = 66.2; H = 7.6 per cent.).

*2-Keto-1-methyl-2:3-dihydro-4-carboline (Ketomethyldihydro-norharman) (Formula XXXIV).*

This interesting substance is obtained when 1-methylindole-2-carboxyacetalamide is warmed with alcoholic hydrogen chloride at 40–45° for a few minutes. The colourless crystals which separate are collected and appear to consist of a hydrochloride, and this must not be washed with alcohol, since it is soluble in alcohol containing hydrogen chloride. If, however, the substance, after draining on porous porcelain, is dissolved in much hot alcohol, ketomethyldihydrocarboline itself separates, on cooling, in long, colourless needles. For analysis, the substance was again crystallised from alcohol (Found: C = 72.7; H = 5.0.  $C_{12}H_{10}ON_2$  requires C = 72.7; H = 5.0 per cent.).

*2-Keto-1-methyl-2:3-dihydro-4-carboline* melts at 242° and is generally more readily soluble in organic solvents than 5-keto-4:5-dihydroindole-diazine (m. p. 247°; p. 1627). Unlike the latter substance, it is appreciably soluble in boiling water. Its basic character is definite although feeble, and it is also phenolic. In both acid and alkaline solution it exhibits blue fluorescence.

*Synthesis of 4-Carboline (Norharman) (Formula II).*

*2-Keto-1-methyl-2:3-dihydro-4-carboline*, finely powdered and intimately mixed with twenty times its weight of pure zinc dust, was cautiously distilled in a stream of hydrogen over a layer of zinc dust about eighteen inches long contained in a hard-glass tube heated in a combustion furnace. The distillate was a pale yellow resin and the portion of the tube containing it was cut out, ground, and extracted with boiling dilute acetic acid with the addition of a little animal charcoal. The filtered solution exhibited intense blue fluorescence, and on the addition of a hot solution of picric acid gave a voluminous precipitate of a picrate. This was collected and recrystallised twice from hot water. The base was then regenerated into ether by means of dilute potassium hydroxide and the ethereal solution well washed with concentrated aqueous potassium hydroxide and dried over the solid reagent. The residue, after removal of the solvent, could be crystallised from benzene and had all the properties of norharman. The melting point was always unsatisfactory, however, and as it seemed probable that this was due to admixture of norharman with its *N*-methyl derivative, the

following procedure was adopted. The base was dissolved in dilute hydrochloric acid, the benzene mother-liquors and the apparatus employed in crystallisations were washed with the same reagent, and the combined solutions were concentrated, and the base precipitated by the addition of ammonia, collected, washed with water, and dried in air. The material was then mixed with a little hydriodic acid ( $d$  1.8) and heated in a test-tube in a sulphuric acid bath to about  $300^{\circ}$ . The process was repeated twice and the product triturated with sulphurous acid, dissolved in hot alcohol, and after the addition of potassium hydroxide diluted with water and extracted with ether. The ethereal solution was washed with aqueous potassium hydroxide and then with water and finally with dilute nitric acid. This acid extract was concentrated on the steam-bath and on cooling the nitrate crystallised in pale yellow needles. The salt was once recrystallised from hot dilute nitric acid and the base was then regenerated and crystallised from benzene. The compound was thus obtained in colourless needles melting at  $198^{\circ}$  and at the same temperature when mixed with a specimen of norharman obtained as described on p. 1619.

*6-Methoxy-3-methylindole-2-carboxylic Acid* (Formula XLIII).

This acid was synthesised from *o*-nitro-*p*-tolyl methyl ether (p. 1629) in a manner similar to that employed in the synthesis of 3-methylindole-2-carboxylic acid from *o*-nitrotoluene (p. 1634). Sodium (4.6 grams), dissolved in alcohol (70 c.c.), was cooled, mixed with ethyl oxalate (14.6 grams) and then *o*-nitro-*p*-tolyl methyl ether (8.3 grams) added. After keeping for three days at  $40^{\circ}$ , the thick, dark red mass was thoroughly mixed with methyl iodide (28 grams) and the whole heated under reflux for twenty-four hours, when the red colour had almost disappeared.

The alcohol and excess of methyl iodide were distilled off under reduced pressure, water was added, and the mass extracted several times with ether. The ethereal extract was washed with water, dried over calcium chloride, and the ether distilled off, when a syrup remained which did not crystallise but evidently consisted of *ethyl  $\alpha$ -keto- $\beta$ -o-nitro-*p*-methoxyphenylbutyrate*,  $\text{MeO} \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{CHMe} \cdot \text{CO} \cdot \text{CO}_2\text{Et}$ . The syrup was dissolved in glacial acetic acid (200 c.c.), and zinc dust (30 grams of 90 per cent.) added with constant shaking at such a rate that the acetic acid almost boiled. When all had been added, the whole was boiled for a few minutes, filtered with the aid of the pump, and water added to the filtrate, when an oil separated, which rapidly solidified, and more was obtained by extracting the zinc precipitate and solution with ether. After draining on porous

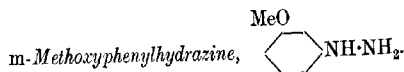
porcelain, the solid was recrystallised from a little alcohol, when colourless crystals were obtained which melted at  $128^{\circ}$  and consisted of *ethyl 6-methoxy-3-methylindole-2-carboxylate*.

This ester is readily soluble in alcohol, sparingly so in benzene, and almost insoluble in light petroleum (Found: C = 67.1; H = 6.3.  $C_{13}H_{15}O_3N$  requires C = 67.0; H = 6.4 per cent.).

This ester was hydrolysed by boiling with methyl-alcoholic potassium hydroxide, water was added, the solution evaporated until free from methyl alcohol and acidified with hydrochloric acid, when *6-methoxy-3-methylindole-2-carboxylic acid* separated as a colourless, crystalline powder, which melted at  $200-202^{\circ}$  without decomposition and in appearance and many of its properties resembled *3-methylindole-2-carboxylic acid* (m. p.  $164^{\circ}$ ; p. 1634).

*6-Methoxy-3-methylindole (6-Methoxyscatole) (Formula XLIV).*

In order to prepare this substance, *6-methoxy-3-methylindole-2-carboxylic acid* contained in a narrow test-tube was heated at about  $210^{\circ}$  by means of a sulphuric acid bath, when it effervesced and a white sublimate of lustrous plates condensed on the sides of the tube. A further quantity was obtained by extracting the rather tarry residue in the tube with boiling, very dilute sodium carbonate solution, the filtered solution, on standing, depositing almost colourless leaflets. The crystalline sublimate melted directly at  $125^{\circ}$  and consisted of *6-methoxy-3-methylindole*, since a mixed melting point showed that it was identical with the substance obtained by the action of heat on *6-methoxy-2-carboxyindole-3-acetic acid* (p. 1641). *6-Methoxy-3-methylindole* has a faint and not unpleasant odour, and is very readily soluble in the usual organic solvents. A splinter of a crystal dissolved in alcohol and mixed with *p*-dimethylaminobenzaldehyde and a drop of hydrochloric acid develops a bluish-green colour, which becomes yellowish green on the addition of more hydrochloric acid. On warming the solution, a rich bluish-purple colour develops, which is changed to deep bluish-violet by a drop of sodium nitrite. A pine shaving moistened with hydrochloric acid is coloured bluish-violet by the substituted indole.



This substance, which had not previously been obtained, was required for the synthesis of the acid described in the next section,

and was prepared from *m*-anisidine by the following process: *m*-Anisidine (61.5 grams) is added to hydrochloric acid (500 c.c. of *d* 1.16), cooled in a freezing mixture and the whole vigorously stirred, when the hydrochloride of the base separates as a thick paste.

Sodium nitrite (150 c.c. containing 0.23 gram per c.c.) is gradually added, the stirring being continued and the whole kept at 0°. A well-cooled solution of stannous chloride (350 grams) in hydrochloric acid (300 c.c.) is run in slowly and after about four hours the heavy, white precipitate is collected, well pressed, and shaken with sodium hydroxide solution (400 c.c. of 25 per cent.) and ether (250 c.c.) and the ethereal layer separated. The aqueous solution extracted twice more with ether, the combined ethereal extracts re dried over potassium carbonate, the ether is distilled off, and the residual oil fractionated under reduced pressure, when *m*-methoxyphenylhydrazine passes over at 166–168°/15 mm. as a colourless oil. On standing in a freezing mixture, this solidifies to a mass of colourless needles, which melt again at room temperature (Found:  $\bar{v}$  = 20.1.  $C_7H_{10}ON_2$  requires  $N = 20.3$  per cent.).

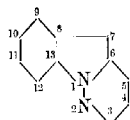
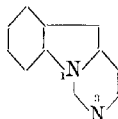
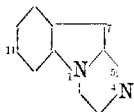
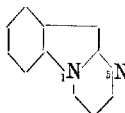
#### 6-Methoxy-2-carboxyindole-3-acetic Acid (Formula XLVI).

As stated in the introduction (p. 1614), this acid is formed when the condensation product of  $\alpha$ -ketoglutaric acid and *m*-methoxyphenylhydrazine is treated with alcoholic hydrogen chloride. *m*-Methoxyphenylhydrazine (4 grams) is dissolved in alcohol (25 c.c.),  $\alpha$ -ketoglutaric acid (4 grams) added, and then gaseous hydrogen chloride passed sufficiently rapidly to raise the alcohol nearly to the boiling point. The liquid becomes brown and then green, ammonium chloride separates, and after two hours the latter is filtered off and most of the alcohol distilled from the filtrate under reduced pressure. On diluting with water, a sticky ester separates, and this is hydrolysed by boiling with methyl-alcoholic potassium hydroxide, water is added, the methyl alcohol removed by distillation under reduced pressure, and the residue acidified, when a sticky mass separates, which is rapidly removed by filtration. On standing, the solution deposits needles which, after recrystallisation from dilute acetic acid, melt at 224–225°. This acid was not analysed owing to the very small yield, but it is evidently 6-methoxy-2-carboxyindole-3-acetic acid, because, when heated, it decomposed with evolution of carbon dioxide and formation of 6-methoxy-3-methylindole (6-methoxyscatole), which melted at 125° and was identical with the substance obtained from 6-methoxy-3-methylindole-2-carboxylic acid by the action of heat (p. 1640).



*Note on Nomenclature.*

There are four theoretically possible heterocyclic types containing fused indole and diazine nuclei, and these isomerides of the carbolines, naphthiminazoles, etc., are figured below. It is suggested that the name "indolediazine" is the most rational description possible, and the system of numbering is similar to that already adopted in the case of the carbolines (compare T., 1919, **115**, 970).

*Indolediazine (1 : 2).**Indolediazine (1 : 3).**Indolediazine (1 : 4).**Indolediazine (1 : 5).*

It should be noted that the numbering is counter-clockwise because the indole nucleus is written



In Richter's "Lexicon" the numbering is usually clockwise, but the result is identical because the indole nucleus is inverted.

We desire to thank Dr. J. Kenyon and Captain J. R. H. Whiston, M.A., for assistance in the preparation of  $\alpha$ -ketoglutaric acid, *o*-nitro-*p*-tolyl methyl ether, and certain other substances required in considerable amount in the course of this investigation. Our thanks are also due to Mr. F. Hall, who carried out a large proportion of the necessary analyses.

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(LXXXVI.—*The Molecular Conductivity of some Sulphonium Compounds in Acetone.*

By SIR PRAPHULLA CHANDRA RÂY and KALIKUMAR KUMAR.

In recent years one of the authors has prepared a large number of new sulphonium compounds which are insoluble in water but are generally soluble in acetone. The acetone solutions of these compounds are fairly good conductors, indicating that the substances behave as salts. An investigation of the conductivity of these compounds was therefore undertaken, with results which are tabulated below. The molecular conductivity increases regularly with dilution and its magnitude is similar to that observed for potassium iodide. These compounds appear, therefore, to be true salts having molecular weights represented by their respective chemical formulæ, and dissociating as uni-univalent electrolytes, possibly into a negative iodine ion and a complex positive ion containing the sulphur chain.

The sulphonium compounds used in the present investigation have already been described (T., 1916, 109, 1, 135, 606; 1919, 115, 551, 1152).

Merek's chemically pure acetone was used. It was further purified by rectification over anhydrous calcium chloride, and had the constant b. p.  $55.8^{\circ}$ ; its specific conductivity was  $3.3 \times 10^{-6}$  reciprocal ohms at  $27^{\circ}$ . The temperatures of the different experiments were between  $26.8^{\circ}$  and  $28.8^{\circ}$ , and the results are expressed for the temperature  $27.8^{\circ}$ .

The results obtained in the conductivity experiments are tabulated below, where  $V$  is the volume in litres containing a gram-molecular weight of the salt.

*Conductivity of Sulphonium Compounds in Acetone Solution at  $27.8^{\circ}$ .*

Compound.	$V = 64$ .	$V = 128$ .	$V = 256$ .	Remarks.
1) $\text{EtMeS}_2\text{MeI}, 2\text{HgI}_2$	—	168.1	181.9	One hexad and one tetrad sulphur atom.
2) $\text{EtS}_2\text{EtI}, 2\text{HgI}_2$ ...	114.5	135.4	144.3	
3) $\text{EtS}_2\text{MeI}, \text{HgI}_2$ .....	124.2	133.6	142.4	One hexad sulphur atom.
4) $\text{EtS}_2\text{EtI}, \text{HgI}_2$ .....	—	125.1	139.4	
5) $\text{EtS}_2\text{PrI}, \text{HgI}_2$ .....	113.3	121.7	136.9	
6) $\text{EtS}_2\text{BuI}, \text{HgI}_2$ .....	113.9 *	120.5	132.3	* At $V = 63.8$ .
7) $\text{MeS}_2\text{MeI}, \text{HgI}_2$ ...	—	110.4	113.0	Chain compound with two tetrad sulphur atoms.
8) $\text{MeS}_2\text{EtI}, \text{HgI}_2$ ...	126.9	140.3	—	
9) $\text{MeP}(\text{EtS}_2)\text{EtI}, \text{HgI}_2$ ...	127.0	139.0	—	
10) $\text{EtS}_2\text{EtI}, \text{HgI}_2$ .....	119.7	132.4	142.8	
11) $\text{PrS}_2\text{MeI}, \text{HgI}_2$ ...	117.6	129.3	140.3	
12) $\text{EtS}_2\text{PrI}, \text{HgI}_2$ .....	112.2	125.3	133.6	
Potassium Iodide .....	—	115.5	130.5	At $25^{\circ}$

## Discussion.

The disulphonium chain compounds with one hexad and one tetrad sulphur atom give the best conducting solutions in acetone. They are followed by the monosulphonium hexad compounds, whilst the disulphonium compounds with two tetrad sulphur atoms give the smallest conductivities, comparable with the values for potassium iodide in acetone solution.

The conductivities of similar compounds diminish, without exception, with increasing molecular weight, for example, on comparing the compounds numbered (1) and (2) it will be found that the replacement of two methyl groups by two ethyl groups lowers the conductivity from 168.1 to 135.4. This relation between conductivity and molecular weight is borne out by the values for the compounds (3), (4), and (5), and those for the compounds (9), (10), and (11).

The compounds (11) and (12) have identical molecular weights, but show an appreciable difference in their conducting power. This is probably due to the relative difference in the magnitude of the aliphatic radicles of the two compounds. Thus the methyl and propyl radicles differ by two methylene groups, whereas ethyl and propyl differ by only one.

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# CLXXXVII.—The Essential Oil from *Andropogon iwarancusa*, Jones, and the Constitution of *Piperitone*.

By JOHN LIONEL SIMONSEN.

FOR some time past the author has been investigating the oil obtained by the distillation of the grass—*Andropogon iwarancusa*, Jones.\* As the main constituent of the oil (approximately 80

\* Mr. R. S. Hole, Forest Botanist, has kindly furnished me with the following botanical note:

## Taxonomy.

In 1889, Hackel described the following forms:

- (1) *Andropogon laniger*, Desf., var. *a genuinus* from Africa, Arabia, and India, var. *β grandiflorus* from Persia.
- (2) *Andropogon iwarancusa*, Blane, var. *a genuinus* from India, var.

per cent.) was found to be a ketone identical apparently with piperitone, it appears desirable, in view of the recent publication of the paper by Smith and Read (this vol., p. 779) dealing with the properties of piperitone, to place on record the results so far obtained, leaving to these authors the further investigation of this interesting ketone.

*Andropogon iwarancusa*, Jones, occurs in the Himalayas and outer hill zone from Kashmir to Assam ascending to 8000 ft. and above; in the plains from North West Himalaya to Bombay Presidency.

The oil from *A. iwarancusa*, Jones, does not appear to have been previously investigated, although the constituents of the oil of the closely related grass, *Cymbopogon sennaarensis*, Chiov., have been examined by Roberts (T., 1915, 107, 1465). The oil used in this research was kindly placed at the disposal of the author by Colonel Johnson of Abbotabad, and had been obtained in a yield of about per cent. by steam distillation in the usual manner. It has been found to be of comparatively simple composition, consisting of a terpene, which has not up to the present been identified and is being further investigated, together with a ketone which has properties agreeing in nearly all respects with those of *dl*-piperitone isolated by Lead and Smith from *Eucalyptus dives* except that it was found to be strongly dextrorotatory ( $[\alpha]_D^{25} + 36.76^\circ$ ). The properties of this ketone would further appear to be identical with those of the ketones isolated by Schimmel & Co. (Report 1910, p. 97) from

*sennaarensis* from Africa, var.  $\gamma$  *proximus* from Africa (DC. *Mon. Phan.*, vol. VI, pp. 598—601).

In 1906, Dr. Stapf pointed out that the correct, original name of (2) was *Andropogon iwarancusa*, Jones (*Kew Bull.*, 1906, p. 314); at the same time he suggested breaking up the large genus *Andropogon* as understood by Hackel, and the definition of Hackel's two Indian plants as distinct species under the names of (1) *Cymbopogon schananthus*, Spreng., and (2) *Cymbopogon iwarancusa*, Schult. (*loc. cit.*, pp. 352—354). Dr. Stapf, however, remarks that "It is not impossible that the distinguishing characters of *C. iwarancusa* as compared with *C. schananthus*, namely, the robust state, the long, flat, and relatively broad leaves, and the more composite panicles, are mainly due to climatic influences," and when speaking of the distribution of *C. schananthus* says "the eastern limit is ill-defined, as here the areas of *C. schananthus* and *C. iwarancusa* overlap, and numerous transition forms occur" (*loc. cit.*, pp. 314, 353). These plants are now being studied at the Forest Research Institute, Dehra Dun, with the object of deciding what forms, if any, are really distinct and can be distinguished by well-marked and constant characters, morphological or chemical, and meanwhile it is believed to be advisable to follow the *Flora of British India*, VII, p. 203, and to deal with the Indian forms of this plant as a single species under the name *Andropogon iwarancusa*, Jones.

Japanese peppermint oil and by Roberts (*loc. cit.*) from *O. serrata arensis*. These authors considered the ketones isolated by them to be identical with  $\Delta^1$ -*p*-menthen-3-one, which had been prepared synthetically by Wallach (*Annalen*, 1908, **362**, 272) from 1:3:4-trihydroxyterpane. This view of the constitution was based (a) on the identity of the properties of the derivatives (semicarbazones and oximes) and (b) on the products of oxidation, namely, thymol, diosphenol,  $\alpha$ -hydroxy- $\alpha$ -methyl- $\beta$ -isopropyladipic acid,  $\gamma$ -acetyl- $\alpha$ -isopropylbutyric acid, and  $\alpha$ -isopropylglutaric acid. The isolation of these products would appear to leave little doubt that these ketones had the constitution assigned to them unless some molecular rearrangement had taken place during the oxidation.

Read and Smith (*loc. cit.*) would appear to consider *dl*-piperitone to be not identical with  $\Delta^1$ -*p*-menthen-3-one, although they point out that it must be a *p*-menthenone, since menthol was formed on reduction and thymol on oxidation with ferric chloride. Although they expressly leave the discussion of the constitution of *dl*-piperitone to a future communication (*loc. cit.*, p. 783), they apparently base their present view that it cannot be identical with any known *p*-menthenone mainly on the fact that on treatment with benzaldehyde in the presence of alkali a benzylidene derivative was formed. They have also recorded melting points for the semicarbazone, oxime, and hydroxylamino-oxime differing somewhat from those given to the similar derivatives of  $\Delta^1$ -*p*-menthen-3-one.

The ketone obtained by the author, apart from its optical activity, had constants agreeing fairly well with those found for *dl*-piperitone and also with those recorded by Wallach (*loc. cit.*) for  $\Delta^1$ -*p*-menthen-3-one. When purified through its sodium sulphite compound, the ketone was almost completely racemised ( $[\alpha]_D^{25} + 7.92^\circ$ ), a fact readily explicable if it is assumed that in the presence of alkali enol formation takes place with consequent loss of the asymmetric carbon atom. This view is supported by the fact that the ketone is also racemised by treatment with dilute alkali and all derivatives prepared in the presence of alkali were found to be optically inactive. The identity of the racemic ketone with *dl*-piperitone would appear to be definitely proved (a) by the formation of a benzylidene derivative, m. p.  $61^\circ$ , and a hydroxylamino-oxime, m. p.  $170$ – $171^\circ$ , (b) by oxidation to thymol with ferric chloride, and (c) by reduction to menthol. On the other hand, a slight divergence from the results obtained by Read and Smith was observed in the melting points of the semicarbazone and oxime. When the ketone was treated with semicarbazide hydrochloride in the usual manner, a mixture of two semicarbazones was obtained; the  $\alpha$ -semicarbazone melted at  $225$ – $227^\circ$  and the  $\beta$ -semicarbazone at  $174$ – $176^\circ$  (Schimmel

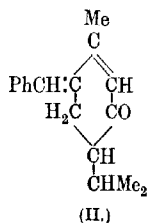
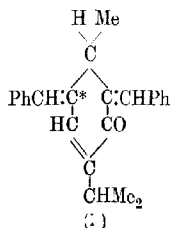
and Co., *loc. cit.*, give 224—225° and 170—171° as the melting points of these two semicarbazones). For the oxime also a somewhat higher melting point has been obtained by the author, namely, 117—118° (Read and Smith give 110—111°). The author would suggest that the somewhat lower melting point for the semicarbazone observed by Read and Smith was due to its not having been quite free from the more fusible isomeride, which the author has found to be removed only with considerable difficulty on crystallisation from alcohol, the solvent used by these authors. By the use of acetic acid, the  $\alpha$ -semicarbazone was obtained pure after two crystallisations. The considerably higher melting point obtained in the case of the oxime is somewhat more difficult to understand, but it is possible that Read and Smith's specimen was contaminated with a trace of the stereoisomeride. Some support is lent to this suggestion in that the author, on one occasion, on boiling the pure oxime (m. p. 117—118°) with an excess of hydroxylamine hydrochloride and sodium acetate for some days with the object of preparing the hydroxylaminoxime, obtained as the product an oxime which was obviously a mixture and melted indefinitely at 90°; analysis established the absence of any impurity and on fractional crystallisation a small quantity of the pure oxime of m. p. 117—118° was separated, but it was not found possible to isolate the stereoisomeride, which was undoubtedly present, in a pure state. On warming the mixture of oximes for some time with a little dilute alkali, the whole was reconverted into the oxime of m. p. 117—118°.

When the active ketone was treated with semicarbazide hydrochloride, in addition to the inactive  $\alpha$ -semicarbazone of m. p. 225—227°, an active  $\beta$ -semicarbazone melting at 193—194° was obtained. As was to be expected in a substance possessing a system of conjugate linkings, the rotatory power was considerably higher than that of the ketone from which it was derived, the rotation at the same time having become negative. Attempts to prepare an optically active oxime were unsuccessful; the active ketone, on treatment with hydroxylamine hydrochloride in the manner found suitable for the preparation of the inactive oxime, yielded an oil from which a small quantity of the inactive oxime could be isolated, whilst if dilute alkali was used in place of sodium acetate to neutralise the hydrochloric acid the inactive oxime was obtained in an excellent yield. An optically active *hydroxylaminoxime acetate* was, however, prepared (see p. 1652).

Reference has already been made to the fact that Schimmel & Co. and Roberts (*loc. cit.*) obtained on oxidation a variety of products which left no doubt as to the constitution of the ketones investigated by them. When the ketone from *A. tiarancusa* oil was oxidised

in ice-cold alkaline solution with potassium permanganate, the main product of the reaction was *l*- $\gamma$ -acetyl- $\alpha$ -isopropylbutyric acid. This acid, which was obtained as an oil, was identified by conversion into its semicarbazone, which melted, as stated by Wallach (*Annalen*, 1910, **379**, 188), at 150–152°. On oxidation of the oily acid with hypobromite solution in the usual manner, a quantitative yield of *dl*- $\alpha$ -isopropylglutaric acid melting at 94–95° was obtained, and this acid showed all the properties assigned to it by Perkin (T., 1896, **69**, 1495).

In the author's opinion, the identity of the ketone obtained from *A. narancausa* oil with piperitone cannot be doubted, and it must be regarded as *d*-piperitone. Further, from a consideration of the products formed on oxidation, there can be no doubt that this ketone is *d*- $\Delta^1$ -*p*-menthen-3-one. The formation of the hydroxyl amino-oxime is in agreement with this view, since, so far as the author is aware, only substances possessing a double linking in the  $\alpha$ -position to the carbonyl group give rise to such compounds. Although it might appear at first sight that the formation of a benzylidene derivative was a cogent argument against such a constitution, yet Wallach (*Annalen*, 1913, **397**, 216) observed that  $\Delta^4$ -*p*-menthen-3-one gave a dibenzylidene derivative, to which he assigned formula I, and he suggested that the formation of this substance was due to activation of the carbon atom\* by the adjacent double linking. A similar argument satisfactorily accounts for the formation of the benzylidene derivative of piperitone, which would then be represented by formula II.



#### EXPERIMENTAL.

The oil used for investigation, which had been obtained in a 1 per cent. yield from the grass, was pale yellow in colour and possessed a characteristic smell of peppermint. It had the following constants:  $D_{20}^{20}$  0.9203,  $n_D^{20}$  1.481,  $[\alpha]_D^{20}$  + 51.68°, acid value 0.7, saponification value 12.0, saponification value after acetylation

17.4,\* (vol.) percentage of ketone by absorption with neutral sodium sulphite solution 77.

A quantity of the oil was distilled under diminished pressure (200 mm.), when the following fractions were obtained: (I) up to 66° (20 per cent.), (II) 160—190° (73.2 per cent.), (III) above 190° (6.6 per cent.). These fractions were systematically refractionated at the same pressure and yielded ultimately the following fractions: (i) 115—130° (14.6 per cent.), (ii) 130—174° (1.6 per cent.), (iii) 174—185° (70 per cent.), (iv) 185—205° (12 per cent.).†

*Fraction (i).*—This fraction consisted essentially of a hydrocarbon (Found: C = 85.8; H = 10.5 per cent.) and had the following constants:  $D_{20}^{20}$  0.8561,  $n_D^{20}$  1.4736,  $[\alpha]_D^{20}$  + 59.95°. It was purified by repeated distillation over sodium and finally over sodium in a current of hydrogen. The hydrocarbon then distilled at 101°/100 mm. and at 163—164°/698 mm., and had  $D_{20}^{20}$  0.8565,  $n_D^{20}$  1.474,  $[\alpha]_D^{20}$  + 54.82° (Found: C = 88.4; H = 11.4.  $C_{10}H_{16}$  requires C = 88.2; H = 11.8 per cent.). The hydrocarbon possessed a pleasant smell reminiscent of cymene; when it was dissolved in acetic anhydride solution and treated with a drop of concentrated sulphuric acid, a transient purple coloration appeared, which rapidly passed into a deep brown. In chloroform solution it acted readily with bromine, but after the addition of 1 molecule bromine the absorption became very slow and hydrogen bromide was evolved. On removing the chloroform in a vacuum, a viscid oil was obtained, which showed no signs of crystallising. Attempts to prepare a crystalline nitrosochloride, nitrosate, and nitrosite were also unsuccessful, only oils being obtained. When the hydrocarbon was treated with hydrogen chloride in ethereal solution, an oil resulted, which was probably a *monohydrochloride* (Found: C = 22.9.  $C_{10}H_{17}Cl$  requires Cl = 20.6 per cent.); with hydrogen

\* As no trace of either esters or alcohols could be detected on chemical examination of the oil, a sample of the pure ketone (from the sodium sulphite compound) was treated in the usual manner for the determination of the saponification value and of the saponification value after acetylation, when the following results were obtained: saponification value 15.3, saponification value after acetylation 36.7. The action of alkali on the ketone has not been investigated, but it is clear that the oil does not contain either esters or alcohols, the apparent saponification value being due to the action of the alkali on the ketone.

† For purposes of comparison a quantity of the oil (100 grams) was shaken with sodium sulphite solution until absorption was complete, when approximately 78 per cent. of the oil was absorbed. The remaining oil was separated and distilled under diminished pressure (200 mm.), when 14 grams of an oil boiling below 130° were obtained. Only 3 grams of an oil boiling above 190° remained, and this still contained traces of the ketone. This method of separation was found to be extremely tedious, as absorption by the sodium sulphite solution was very slow.



bromide in acetic acid solution, a viscous oil was obtained, which was evidently a *dihydrobromide* (Found: Br = 53.8.  $C_{10}H_{18}Br_2$  requires Br = 53.8 per cent.); the hydrogen iodide derivative was very unstable, and decomposed even when kept at 0°.

The terpene was readily attacked when treated with potassium permanganate at 0° in the presence of alkali. A small quantity of a neutral oxidation product was isolated as a viscous oil which showed no tendency to crystallise. No crystalline acids could be obtained. Further experiments are in progress with a view to determine the constitution of this terpene.

*Fraction (ii).*—This fraction, which was too small in quantity for detailed examination, consisted apparently mainly of a mixture of *d*-piperitone and the hydrocarbon.

*Fraction (iii).*—This fraction, which formed the main bulk of the oil, distilled very constantly at 178–181°/200 mm. and was evidently homogeneous (Found: C = 78.2; H = 10.2.  $C_{10}H_{16}$  requires C = 78.9; H = 10.3 per cent.). The following constants were observed:  $D_{20}^{20}$  0.9321,  $n_D^{20}$  1.481,  $[\alpha]_D^{20} + 36.76^\circ$ . It was almost completely absorbed by a neutral sodium sulphite solution, only about 2 per cent. remaining undissolved. A quantity of the ketone was therefore purified by solution in sodium sulphite solution and reprecipitation by alkali, when it was found to boil at 180–181°/200 mm. and at 230–231°/697 mm. (Found: C = 79.1; H = 10.4 per cent.), and to have  $D_{20}^{20}$  0.9307,  $n_D^{20}$  1.481,  $[\alpha]_D^{20} + 7.92^\circ$ . Attention has already been directed to the racemisation of *d*-piperitone by alkali. *d*-Piperitone is a colourless, mobile oil with a pronounced odour of peppermint; on standing, it gradually becomes brownish-yellow in colour.

*Fraction (iv).*—This fraction still contained a considerable quantity of *d*-piperitone. When this was removed by treatment with semicarbazide hydrochloride, the oil remaining was found to be too small in quantity for examination.

#### *d*-Piperitonesemicarbazone.

For the preparation of the semicarbazone the ketone was mixed with a slight excess of an aqueous solution of semicarbazide hydrochloride, and after the addition of sodium acetate alcohol was added until a clear solution was just obtained. After standing over-night, a copious precipitate of the nearly pure *dl*- $\alpha$ -semicarbazone had crystallised. This was collected (yield 75 per cent.), and after being crystallised twice from acetic acid, in which it was not very readily soluble, was obtained in small, glistening plates which melted at 225–227° (Found: N = 20.4.  $C_{11}H_{19}ON_3$  requires

N = 20.1 per cent.). The melting point was found to be somewhat dependent upon the rate of heating, since when introduced into a bath previously heated at 215° the compound decomposed at 230°. The  $\alpha$ -semicarbazone was found to be very sparingly soluble in all the ordinary organic solvents and to be optically inactive.

The alcoholic solution from which the  $\alpha$ -semicarbazone had separated was diluted with water, when a further quantity of semicarbazone was precipitated. This was purified by repeated crystallisation from alcohol, from which it was ultimately obtained as glistening needles which melted at 193–194°, sintering slightly at 188° (Found: N = 20.3.  $C_{11}H_{19}ON_3$  requires N = 20.1 per cent.).

*d*-Piperitone- $\beta$ -semicarbazone appeared to be somewhat more soluble in alcohol than the racemic  $\beta$ -semicarbazone. When exposed to the air in bright sunlight, it rapidly became yellow, but when kept in the dark the colour developed much more slowly. When dissolved in alcohol, the yellow semicarbazone yielded a colourless solution. The *d*- $\beta$ -semicarbazone was highly active; in pyridine solution  $[\alpha]_D^{25} = -216.3^\circ$  was observed.

#### *dl*-Piperitonesemicarbazones.

The semicarbazones of the racemic ketone were prepared in the manner described above. The *dl*- $\alpha$ -semicarbazone, after crystallisation from acetic acid, melted at 225–227° (Found: N = 20.2 per cent.). The *dl*- $\beta$ -semicarbazone separated from alcohol in stellate masses of needles melting at 174–176° and was optically inactive (Found: N = 20.0 per cent.).

#### *d*-Piperitoneoxime and *d*-Piperitonehydroxylaminoxime Acetate.

For the preparation of the oxime the method advocated by Lapworth and Steele (T., 1911, 99, 1884) was adopted. The active ketone (5 grams) was dissolved in alcohol (20 c.c.) and after the addition of hydroxylamine hydrochloride (2.3 grams) and sodium acetate (4 grams) the mixture was heated on the water-bath for five hours. On distillation in steam, almost the whole of the product passed over, only a small quantity of resinous material remaining in the distillation flask. The steam distillate consisted of an oil which, on long standing at 0°, partly solidified. The solid was separated with the aid of the pump, drained on porous porcelain, and recrystallised from dilute methyl alcohol, when it was obtained in lustrous prisms melting at 117–118° (Found: VOL. CXIX.

$N = 8.7$ .  $C_{10}H_{17}ON$  requires  $N = 8.4$  per cent.). The oxime was optically inactive. The oil from which the solid oxime had been separated was taken up with ether, the ether dried and evaporated, and the residual oil distilled under diminished pressure (100 mm.), when it distilled almost completely at about  $190-195^\circ$ , yielding a viscid oil which deposited a further trace of the solid oxime on standing. The oil was not further investigated, but consisted possibly of the active oxime. When the calculated quantity of sodium hydroxide was used in place of sodium acetate in the preparation of the oxime, similar results were obtained, the yield of solid oxime being slightly higher. If excess of sodium hydroxide was used, only the solid oxime was obtained, the oily oxime being completely absent.

When *d*-piperitone was treated with a considerable excess of hydroxylamine hydrochloride under conditions similar to those described above, a substance was obtained which was not readily volatile in steam. This was purified by crystallisation from a mixture of methyl alcohol and benzene, when it was obtained in long, thin prisms which decomposed at  $156-157^\circ$  (Found:  $C = 55.3$ ;  $H = 9.2$ ;  $N = 11.2$ .  $C_{12}H_{24}O_4N_2$  requires  $C = 55.4$ ;  $H = 9.2$ ;  $N = 10.8$  per cent.). This substance was evidently the *acetate* of *d*-piperitonehydroxylamino-oxime. It was distinctly active and gave in methyl-alcoholic solution  $[\alpha]_D^{20} = 20.42^\circ$ . Attempts to isolate the *d*-piperitonehydroxylamino-oxime in a crystalline form were unsuccessful.

*dl*-Piperitoneoxime and *dl*-Dibromopiperitoneoxime.

When *dl*-piperitone was treated with hydroxylamine hydrochloride in the manner described above, the product in the steam distillate crystallised completely, no trace of an oil being observed. It was purified by crystallisation from dilute methyl alcohol, when it was obtained in lustrous prisms melting at  $117-118^\circ$  (Found:  $N = 8.7$  per cent.).

When the oxime was dissolved in chloroform and treated with the calculated quantity of bromine, *dl*-dibromopiperitoneoxime was readily obtained. It crystallised from alcohol in prisms, or from a dilute solution in cubes, which decomposed at  $141^\circ$  (Found:  $Br = 48.6$ .  $C_{10}H_{17}ONBr_2$  requires  $Br = 48.9$  per cent.).

*dl*-Piperitonehydroxylamino-oxime.

On treatment with excess of hydroxylamine hydrochloride in the manner described by Read and Smith (*loc. cit.*, p. 783) *dl*-piperitone-

hydroxylamino-oxime was obtained. After crystallisation from a mixture of alcohol and ether, it melted at 170–171° and gave all the colour reactions mentioned by these authors (Found: C = 59.6; H = 10.1. Calc., C = 59.9; H = 10.1 per cent.).

*Benzylidene-dl-piperitone.*

This substance was prepared in the manner described by Read and Smith (*loc. cit.*, p. 785). It melted at 61° and had all the properties recorded by these authors (Found: C = 84.4; H = 8.4. Calc., C = 84.9; H = 8.4 per cent.). Although prepared from the optically active ketone, it was found to be inactive.

*Oxidation of d-Piperitone.*

I. *With Ferric Chloride.*—When *d*-piperitone was heated on the water-bath with excess of ferric chloride in acetic acid solution, thymol was obtained in a yield of about 25 per cent. The thymol obtained melted at 50–51° and was identified by the method of mixed melting point and by the usual tests.

II. *With Potassium Permanganate.*—In one experiment *d*-piperitone (50 grams) was mixed with dilute sodium hydroxide solution and treated with a 5 per cent. solution of potassium permanganate at 0° until no further action took place. The solution was filtered, concentrated, and acidified, when a viscous oil separated. This was taken up with ether, the ether dried and evaporated, and the residual oil esterified in the usual manner. The ethyl ester thus obtained distilled mainly at 170–180°/53 mm. and consisted apparently of nearly pure ethyl *l*- $\gamma$ -acetyl-*x*-isopropylbutyrate, since on analysis it gave figures agreeing approximately with this formula (Found: C = 64.6; H = 9.4. Calc., C = 67.3; H = 9.5 per cent.). The ester was found to be slightly active,  $[\alpha]_D^{20}$  = 5.58°. The above view of the constitution was confirmed by the preparation of the *semicarbazone*, which separated from dilute alcohol in woolly needles melting at 115° (Found: N = 16.1.  $C_{12}H_{23}O_3N_3$  requires N = 16.3 per cent.). The crude ester was hydrolysed with alcoholic potassium hydroxide solution and the resulting acid distilled under diminished pressure (48 mm.), when the main portion distilled at 195–200° and consisted of apparently pure *l*- $\gamma$ -acetyl-*x*-isopropylbutyric acid (Found: in the silver salt, Ag = 38.8. Calc., Ag = 38.7 per cent.). The *semicarbazone*, prepared in the usual manner, separated as an oil which rapidly solidified. It was purified by repeated crystallisation from hot water containing a little alcohol, when it was obtained in balls of needles melting at 150–

152°, the melting point depending somewhat on the rate of heating (Found: N = 18.5. Calc., N = 18.3 per cent.). When the compound was treated with sodium hypobromite solution at 0°, a quantitative yield of  $\alpha$ -isopropylglutaric acid was obtained. This acid, after crystallisation from hydrochloric acid, melted at 94–95° (Found: C = 55.4; H = 7.8. Calc., C = 55.2; H = 8.0 per cent.). The acid was found to be optically inactive. The identity of the acid was confirmed by the preparation of the anhydride, which crystallised in needles resembling glass-wool, melted at 53–54°, and gave an anil melting at 158° (compare Perkin, *loc. cit.*).

In conclusion, the author wishes to thank his assistants, Mr. Gopal Rau and Mr. Ghose, for making the analyses.

THE FOREST RESEARCH INSTITUTE,  
DEHRA DUN.

[Received, August 23rd, 1921.]

### CLXXXVIII.—*The Calculation of the Colour of "Cyclic" Coloured Substances.*

By JAMES MOIR.

FOR the purpose of this paper, a "cyclic" coloured substance is to be considered as one which possesses a sharp absorption band caused in some manner by an "active" ring existing in the substance. A ring is "active" if it bears, in any position, an ionisable group of the auxochrome type, namely, OH, NH<sub>2</sub>, NHMe, etc.

The position of the absorption band may vary between  $\lambda$  100 and  $\lambda$  1600 micromillimetres. Some "cyclic" coloured substances, therefore, may appear to be colourless to the eye, which only detects colours the bands of which lie above  $\lambda$  350 and below  $\lambda$  770.

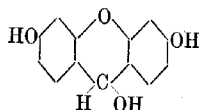
If only one of the rings present in a compound is "active," it is classed as a "monocyclic" coloured substance. In a certain sense, phenol in the presence of alkali and aniline in the presence of acid comply with this definition, but as a rule the absorption band is not fully developed (visible in very great dilution) unless another atom of some kind is attached to the active ring, as, for example, in saligenin and benzoquinone.

Coloured substances with more than one "active" ring are all classed as "dicyclic."\* The simplest type of the linking of two active rings occurs in benzhydrols and indamines. In the more

\* See page 1663.

complex types, there are two linking atoms uniting the active rings, as in the oxazines, fluoresceins, acridines, etc.

Some examples will serve to make these definitions clear. Thus hydroxybenzhydrol,  $C_6H_5 \cdot CH(OH) \cdot C_6H_4 \cdot OH$ , is monocyclic because the simple phenyl ring is not active, whereas dihydroxybenzhydrol,  $HO \cdot C_6H_4 \cdot CH(OH) \cdot C_6H_4 \cdot OH$ , and dihydroxyxanthhydrol,



are "dicyclic," the active rings of the former being singly linked, by  $-CH(OH)-$ , and of the latter doubly linked, by  $-CH(OH)-$  and  $-O-$ .

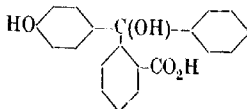
The author has discovered that the position of the absorption band can be calculated from the constitutional formula of the substance in all these cases. The calculation consists merely in multiplying a fundamental wave-length (which is that of the absorption band of the parent-substance) by a number of factors, each of which is constant and characteristic of the group or radicle to which it belongs. This may be expressed by the equation :

$$\lambda_x = k_1 k_2 \dots k_n \lambda_0,$$

in which  $\lambda_0$  is the wave-length of the absorption band of the parent-substance,  $\lambda_x$  that of the substance to be calculated,  $k_1$  the colour-factor (say) for phenyl if the substance is a phenyl derivative of the parent-substance,  $k_2$  the colour-factor for another group or atom (for example, bromine or carboxyl) present in the substance, and so on.

For the monocyclic series, the parent-substance may be taken to be *p*-hydroxybenzyl alcohol, of which the anhydride is quinomethane (methylene-*p*-benzoquinone). This is assumed to have  $\lambda_0 = 290$ . I have not observed it, but the phenoxide ion has  $\lambda_{286}$  and the *p*-tolylxide ion  $\lambda_{287}^*$  in aqueous solution.

The colour of hydroxydiphenylphthalide, as an example of a monocyclic coloured substance, may be calculated. When the formula is written in its hydroxylated form to avoid quinonoid linkings,



\* Baly and Ewbank (T., 1905, 87, diagrams on pp. 1350 and 1352) find  $\lambda_{290}$  and  $291$  in alcohol. The difference is due to the sodium not being ionised.



# PROCEEDINGS

## OF THE

### CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, October 6th, 1921, at 8 p.m., Dr. M. O. FORSTER, F.R.S., Treasurer, in the Chair.

Reference was made to the loss sustained by the Society, through death, of the following Fellows :

	Elected.	Died.
David Brown .....	Mar. 17th, 1870	June 21st.
Francis William Buckland Cunningham .....	Feb. 15th, 1917	July, 1920
Charles Esteourt .....	Feb. 2nd, 1865	June 24th
Tribhuvandas Kalyandas Gajjar .....	Dec. 5th, 1901	—
Henry Tresawna Gerrans .....	Feb. 21st, 1895	June 20th
Edward Gumersall .....	Dec. 4th, 1902	May 18th
Harold Edward Pollock Hodson .....	May 15th, 1913	Sept. 2nd
Ernest James Hoy .....	Dec. 2nd, 1915	July 5th
Henry Rondel Le Sueur .....	Feb. 21st, 1895	July 9th
Frederic Richard Mallet .....	May 7th, 1885	June 24th
Henry Stephen Martin .....	Feb. 20th, 1913	Mar. 16th
John William Reginald Youll .....	Dec. 5th, 1918	July 6th

Certificates were read for the first time in favour of :

Harry Anderson, B.A., 9, Mill Street, Oakham.  
 Francis Bartlett Arnold, 23, Stratford Road, Thornton Heath.  
 Hugh Chester Bell, M.A., Guy's Hospital Medical School, S.E. 1.  
 Frederick John Berry, 51, Reynolds Street, Neutral Bay, Sydney, N.S.W.  
 Jagadish Chandra Bhowmik, M.Sc., 72, Harrison Road, Calcutta.  
 Joseph Roy Boer, B.Sc., 7, Gabriel Street, Honor Oak Park, S.E. 23.  
 Frederick George Braithwaite, Messrs. Lever Bros. (S.A.), Ltd., Durban.  
 William Arthur Percival Challenger, M.Sc., Glenwood, Alkington Road, Whitchurch.  
 Philibert Camille Chaumeton, B.Sc., A.I.C., Messrs. Duroglass, Ltd., 92, Fore Street, E.C. 2.  
 George Henry Croft, M.Sc., 13, Lowther Street, York.  
 David Richard Dawkins, B.Sc., Llwynedyn, Wern Road, Skewen, Neath.  
 Cecil Whitfield Davies, B.Sc., A.I.C., 135, Copers Cope Road, Beckenham.  
 Geoffrey Fairrie, Rosslyn, Merrilocks Road, Blundellsands, Liverpool.



- Robert Allen Fitzsimons, B.Sc., 43, King Henry's Road, Hampstead, N.W.  
 Percy James Fullerton, 107, Macoma Road, Plumstead, S.E. 18.  
 William Buchanan Gray, Box 663, Johannesburg.  
 Solomon Greenberg, A.I.C., 41, Frithville Gardens, W. 12.  
 Leslie Hall, B.Sc., 87, College Road, Isleworth.  
 Percy Charles Haywood, M.Sc., 3, Gladstone Road, Wimbledon, S.W. 19.  
 Harold Robert Hellyer, 140, Elizabeth Street, Sydney.  
 Gwendolen Hindes, B.Sc., Wesley Manse, Barlow Street, Oldham.  
 Cyril Norman Hinshelwood, B.A., Balliol College, Oxford.  
 George Ingham, B.A., A.I.C., Messrs. Kynochs, Ltd., Umbogintwini, Natal.  
 Kenneth James Isaac, 42, Nicoll Road, Harlesden, N.W. 10.  
 Geraldine Zarika Lee Le Bas, B.Sc., Imperial Club, Dover Street, W. 1.  
 Alexander Bernard Manning, M.Sc., 102, Fordhook Avenue, Ealing Common, W. 5.  
 John Henry Middleditch, 15, Fonthill Road, Hove, Brighton.  
 James Gibb Mitchell, B.Sc., Laurelbank, Cupar.  
 George Norman Nicklin, M.A., 9, Willis Road, Cambridge.  
 John Griffith Peake, Erskine, Prospect Road, Summer Hill, Sydney.  
 John Robert Pickering, 113, Mayola Road, Lower Clapton, N.E. 5.  
 Norman Ratcliffe, F.I.C., Messrs. The Glaxo Manufacturing Co., Hamilton, N.Z.  
 Thomas Harold Reade, B.A., M.Sc., A.I.C., 118, Tottenhall Road, Wolverhampton.  
 William Reversion, Philomet, Pelham Road, Bexley Heath.  
 Hugh Medwyn Roberts, B.Sc., A.I.C., Hendy, Crescent Road, Blyth.  
 Kasinath Saikia, B.A., Elvestone, Shillong, Assam.  
 Horace Leonard Saunders, B.Sc., A.I.C., 177, Chepstow Road, Newport, Mon.  
 Schachno Peisach Schotz, D.Sc.Tech., B.Sc., F.I.C., 112, Wellington Road South, Hounslow.  
 William George Shilling, The Mill, Preston Village, Faversham.  
 Walter William Sirman, B.Sc., 222, Reddings Lane, Hall Green, Birmingham.  
 George Paterson Storer, A.I.C., 48, Llanthwy Road, Newport, Mon.  
 Enoch Swan, B.Sc., 129, Liverpool Road, Birkdale, Southport.  
 Walter Thomas, 24, Richborough Road, Cricklewood, N.W. 2.  
 Stanley Horwood Tucker, Lincoln College, Oxford.  
 Edith Hilda Usherwood, B.Sc., 10, Holly Park Gardens, Finchley, N. 3.  
 William Mansergh Varley, M.A., D.Sc., Ph.D., 7, Preston Park Avenue, Brighton.  
 Panna Lal Verma, B.Sc., University College, Dundee.  
 Bertram Thomas Watson, 36, Coopersale Road, Hemerton, E. 9.  
 James Henry Wilkinson, 18, Stockton Road, Sunderland.  
 Bernard Howell Wilson, Jr. A., B.Sc., Lyallpur, Punjab.  
 Percival Harry Woodnoth, 88, Rodenhurst Road, Clapham Park, S.W. 4.

The following papers were read :

- "A new adjustable thermostat for all temperatures between 0° and 100°." By S. J. LEWIS and F. M. WOOD.  
 "The separation of miscible liquids by distillation. Laboratory still-heads." By A. F. DUTTON.  
 "The separation of miscible liquids by distillation. A continuous laboratory still." By A. F. DUTTON.

"The action of diazo-salts on aromatic sulphonamides. Part I."

By P. K. DUTT, H. R. WHITEHEAD, and A. WORMALL.

"Neutral salt action on the hydrolysis of ethyl formate." By A. B. MANNING.

"Synthetic optical activity." By A. SHIMOMURA and J. B. COHEN.

"The mechanism of the action of fused alkalis. Part II. Action of fused potassium hydroxide on phenylglyceric acid." By (the late) H. R. LE SUEUR and C. C. WOOD.

Ordinary Scientific Meeting, Thursday, October 20th, 1921, at 8 p.m., SIR JAMES WALKER, D.Sc., LL.D., F.R.S., President, in the Chair.

The PRESIDENT referred to the loss sustained by the Society, through death, of :

	Elected.	Died.
Edward John Bevan .....	Mar. 1st, 1883	Oct. 17th
Sir Edward Chaning Wills .....	May 7th, 1896	Oct. 14th

The PRESIDENT announced :

(1) That the Council had appointed Dr. J. Irvine Masson to fill the vacancy in the office of Secretary caused by the death of Dr. I. R. Le Sueur.

(2) That up to the present the sum of £106 18s. 6d. had been received for the Russian Fund, and various gifts of clothing. The first consignment of clothing and a small sum will shortly be sent to the Secretary of the Helsingfors University Committee for distribution amongst Russian scientific men.

Certificates were read for the first time in favour of :

George Norman Burkhardt, B.Sc., Hulme Hall, Victoria Park, Manchester.

Harold Eben Carr, Lynton, St. Augustine's Avenue, S. Croydon.

John Stanley Carter, Holly Farm, Farnley, Leeds.

Laurence Hepburn Cocks, The Holme, Ashted, Epsom.

Frank Dickens, B.A., 37, Cale Street, Chelsea, S.W. 3.

Gazim Fakhoury, The University, Edgbaston, Birmingham.

Gilbert Greenwood, B.Sc., Thorn Bank, Edenfield, Manchester.

George Herbert Griffiths, 23, Drummond Road, Hoxlake, Birkenhead.

Harold Joseph Hailstone, The Gas Works, Rochdale.

Ernest Sydney Hedges, B.Sc., Blenheim, Albert Avenue, Sedgeley Park, Prestwich, Manchester.

Vilfred Alec Hodsdon, Springfields, Bexley, Kent.

Frederick Montgomery Low, 1 Woodstock Road, Bedford Park, W. 4.

James Nicol, 12, Vectis Road, Tooting, S.W. 17.

David Arthur Ruell, B.Sc., 17, Thornton Street, West Hartlepool.

Frederic Wooler Simpson, Cheapside, Spennymoor, Co. Durham.

Samuel Smith, University College, Gower Street, W.C. 1.

Edmund Wyndham Whitefield, A.I.C., Gordon College, Khartoum.

James George Wilkie, 11, Luxemburg Gardens, Hammersmith, W. 6.

The following papers were read :

- "Nitro- and amino-derivatives of 4-phenylglyoxaline." By R. L. GRANT and F. L. PYMAN.  
 "Chenopodium oil." By T. A. HENRY and H. PAGET.  
 "Some further experiments in a new method for the determination of molecular weights." By P. BLACKMAN.  
 "The reversibility of the Michael reaction." By C. K. INGOLD and W. J. POWELL.

### RESEARCH FUND.

A meeting of the Research Fund Committee will be held in December next. Applications for Grants, to be made on forms obtainable from the Assistant Secretary, The Chemical Society, Burlington House, W. 1., must be received on or before Thursday, December 1st, 1921.

All persons who received Grants in December, 1920, or in December of any previous year, whose accounts have not been closed by the Council, are reminded that reports must be returned by December 1st.

### ADDITIONS TO THE LIBRARY.

#### I. Presented by Sir J. J. Dobbie.

(a) Ten pamphlets and reprints of papers by Professor John Ferguson, including the following not already contained in the Library.

FERGUSON, JOHN. Bibliographical notes on the English translation of Polydore Vergil's work "De inventoribus rerum." (From *The Archaeologia*, 1888, 51.)

— Bibliographical notes on histories of inventions and books of secrets. Parts IV—VI. (From the *Trans. Archaeol. Soc. Glasgow*, 1888—1890.)

— Bibliographical note on the "De triumpho stultitiae" of Perisaulus Faustinus. (From *The Library*, 1890.)

— Bibliographia Paracelsica. Contributions towards a knowledge of Paracelsus and his writings. Part III. Glasgow 1890. pp. 66.

(b) Fifty-three pamphlets and reprints of papers by Sir William Ramsay, including the following not already contained in the Library.

RAMSAY, SIR WILLIAM. Investigations on the toluic, and nitro-toluic acids. Inaugural dissertation for the attainment of the degree of Doctor of Natural Sciences. Tübingen 1872. pp. 27.

- RAMSAY, SIR WILLIAM. On smell. [London 1882.] pp. 14.  
 — Universities abroad. (From the *Times*, June 8—9, 1892.)  
 — University extension lectures. Syllabus of a course of twenty-five lectures on the history of chemical discovery. London 1895. pp. 15.  
 — Education in science in Britain and in Germany. Address delivered . . . at the opening ceremony of the session 1896—97, September 30th, 1896, University College of North Wales, Bangor. Bangor 1896. pp. 19.  
 — The inert constituents of the atmosphere. (From the *Popular Sci. Monthly*, 1901.)  
 — Einige Betrachtungen über das periodische Gesetz der Elemente. (From the *Verh. Ges. deut. Naturforsch. Ärzte*, 1903.)

## II. Miscellaneous Donations.

AUDEN, HAROLD ALDEN. Sulphur and sulphur derivatives. London [1921]. pp. xviii + 101. ill. 3s. net. (*Recd.* 9/9/21.)

From the Publishers: Sir Isaac Pitman & Sons.

BARNETT, EDWARD DE BARRY, and THORNE, PERCY CYRIL LESLEY. Organic analysis: qualitative and quantitative. London 1921. pp. xii + 168. ill. 7s. 6d. net. (*Recd.* 4/10/21.)

From the Publishers: The University of London Press.

BHAGWAT, VINAYAK KESHAV. Calculations in organic chemistry. Bombay 1921. pp. xii + 138. (*Recd.* 15/8/21.)

From the Author.

BRITISH OPTICAL INSTRUMENT MANUFACTURERS' ASSOCIATION. Dictionary of British scientific instruments. London 1921. pp. xii + 334. ill. (*Reference.*) 21s. net. From the Association.

BUREAU OF BIO-TECHNOLOGY. Bulletin. No. 1 etc., Leeds 1920+. ill. (*Reference.*) From the Bureau.

CROSSHAW, HARRY BRENNAN. Silver ores. (Imperial Institute Monograph on Mineral Resources.) London 1921. pp. 152.

From the Director.

CURIOSITIES IN CHYMISTRY: being new experiments and observations concerning the principles of natural bodies. Written by a Person of Honour, and published by his operator, H. G. London 1691. pp. [vi] + 113. (*Reference.*) From Dr. A. Scott.

EGYPT. Department of Public Health. Reports and notes of the Public Health Laboratories, Cairo. No. 4. Nutritive values and characters of rations issued to officials . . . of the Egyptian Government. Cairo 1921. pp. vi + 57. P. T. 20. (*Recd.* 19/7/21.)

From the Department.

FARMER, ROBERT CROSBIE. Industrial and power alcohol: the sources, production, and denaturing of alcohol—its manifold chemical and physical applications in industries and manufactures, and its use as a fuel for internal combustion engines—technical, commercial, and excise aspects of the problem. London 1921. pp. x + 110. ill. 2s. 6d. net. (*Recd.* 19/8/21.)

From the Publishers: Sir Isaac Pitman & Sons.

FIERZ-DAVID, HANS EDUARD. Reise durch einige Industriegebiete der Vereinigten Staaten von Nord-Amerika, September–November 1920. Zürich 1921. pp. 79. ill. (*Recd.* 7/10/21.)

From the Author.

GENEESKUNDIG LABORATORIUM TE WELTEVREDEN. Mededeelingen. 3rd Series A. 1917–18 etc., Weltevreden 1918+. (*Reference*) ill.

From the Director.

GOWLAND, WILLIAM. The metallurgy of the non-ferrous metals. 3rd edition. London 1921. pp. xxxii + 632. ill. 30s. net. (*Recd.* 30/9/21.)

From the Author.

IMPERIAL INSTITUTE. Indian Trade Enquiry. Reports on jute and silk. London 1921. pp. x + 90. 5s. net. (*Recd.* 4/10/21.)

From the Director.

— — — Reports on timbers and paper materials. London 1921. pp. x + 57. 4s. net. (*Recd.* 15/8/21.)

From the Director.

KAY, SYDNEY ALEXANDER. A text-book of qualitative analysis of inorganic substances. London 1921. pp. viii + 80. ill. 7s. 6d. net. (*Recd.* 4/10/21.) From the Publishers: Messrs. Gurney & Jackson.

LAMPADIUS, WILHELM AUGUST. Handbuch der chemischen Analyse der Mineralkörper. Freyburg 1801. pp. viii + 364. ill. (*Reference*.)

From Professor P. Phillips Bedson.

— — — Beiträge zur Erweiterung der Chemie und deren Anwendung auf Hüttenwesen, Fabriken und Ackerbau. Vol. I. Freyburg 1804. pp. viii + 342. ill. (*Reference*.) From Professor P. Phillips Bedson.

MOUREU, CHARLES. Fundamental principles of organic chemistry. Translated from the 6th French edition by WALTER T. K. BRAUNHOLTZ. London 1921. pp. xviii + 400. 12s. 6d. net. (*Recd.* 15/8/21.) From the Publishers: Messrs. G. Bell & Sons.

ODLING, WILLIAM. Chemistry. London [1883]. pp. vi + 126. (*Recd.* 7/9/21.)

From Mrs. Mary B. Odling.

PARKINSON, JAMES. The chemical pocket-book, or memoranda chemica; arranged in a compendium of chemistry, according to the latest discoveries, with Bergman's table of single elective attractions, as improved by Dr. G. Pearson. Calculated, as well for the occasional reference of the professional student, as to supply others with a general knowledge of chemistry. London 1800. pp. xii + 1—169, \*152—\*169, 170, 169—216. (*Reference*.)

From Professor P. Phillips Bedson.

PATTERSON, AUSTIN M. A French-English dictionary for chemists. New York 1921. pp. xviii + 384. (*Reference.*) 18s. net.

From the Publishers: Messrs. Chapman & Hall.

PAVENTA, E. F. Italian technical words and phrases: an English-Italian and Italian-English dictionary of technical and business terms and phrases. London 1921. pp. 308. (*Reference.*) 6s. net.

From the Publishers: Messrs. E. Marlborough & Co.

PREFFER, W. Osmotische Untersuchungen: Studien zur Zellmechanik. 2nd edition. Leipzig 1921. pp. xiv + 236. ill. (*Recd.* 26.9.21.)

From the Publisher: Wilhelm Engelmann.

REVUE CHIMIQUE. Časopis za čistu kemiju i za sve grane primenjene kemije. Vol. I, etc. Zagreb 1921+. (*Reference.*)

RICHARDSON, WILLIAM. The chemical principles of the metallic arts. Birmingham 1790. pp. civ + 205. (*Reference.*)

From Professor P. Phillips Bedson.

ROAF, HERBERT ELTON. Biological chemistry. London [1921]. pp. xvi + 216. ill. 10s. 6d. net. (*Recd.* 28.9.21.)

From the Author.

SEXTON, ALEXANDER HUMBOLDT. Fuel and refractory materials. New edition. By WILLIAM BROWN DAVIDSON. London 1921. pp. [x] + 382. ill. 12s. 6d. net. (*Recd.* 4.10.21.)

From the Publishers: Messrs. Blackie & Son.

UNITED STATES DEPARTMENT OF COMMERCE. *Bureau of the Census*. Abstract of the census of manufactures, 1914. Washington 1917. pp. 722. (*Reference.*) From Mr. R. N. Garrod Thomas.

WEYL, THEODOR [Editor]. Die Methoden der organischen Chemie. 2nd edition. Edited by JOSEF HOUBEN. Vol. I. Leipzig 1921. pp. xxvii + 1121. ill. (*Recd.* 11.7.21.)

From the Publisher: Georg Thieme.

WHITMORE, FRANK C. Organic compounds of mercury. New York 1921. pp. 398. 84.50. (*Recd.* 15.8.21.)

From the Publishers: Chemical Catalog Company.

### III. By Purchase.

BERTHOLLET, CLAUDE LOUIS, and BERTHOLLET, AMÉDÉE B. Elements of the art of dyeing and bleaching. New edition. Translated by ANDREW URE. London 1841. pp. xvi + 540. ill. (*Reference.*)

BOLAS, BERNARD D. A handbook of laboratory glass-blowing. London 1921. pp. viii + 106. ill. 3s. 6d. net. (*Recd.* 18.6.21.)

BURGESS, CHARLES F., PULSIFER, H. B., and FREUD, BENJAMIN B. Applied electrochemistry and metallurgy: a practical treatise on commercial chemistry, the electric furnace, the manufacture of

ozone and nitrogen by high-tension discharges, and the metallurgy of iron, steel, and miscellaneous metals. Chicago 1920. pp. viii + 198. ill. 17s. net. (*Recd.* 15/8/21.)

COFFIGNIER, CH. Les vernis. Paris 1921. pp. viii + 640. ill. 40fr. (*Recd.* 15/6/21.)

COMBY, ARTHUR MESSINGER, and HAHN, DOROTHY A. A dictionary of chemical solubilities—inorganic. 2nd edition. New York 1921. pp. xx + 1142. 72s. net. (*Reference.*)

DEUTSCHER FÄRBER-KALENDER. Wittenberg 1921. pp. 221. ill. (*Reference.*)

FRITSCH, J. Les huiles industrielles et leurs dérivés. Paris 1920. pp. viii + 357. ill. 17s. 6d. (*Recd.* 22/6/21.)

HAUSBRAND, E. Die Wirkungsweise der Rektifizier- und Destillier. Apparate mit Hilfe einfacher mathematischer Betrachtungen. 4th edition. Berlin 1921. pp. x + 270. ill. (*Recd.* 15/7/21.)

LEHMANN, OTTO. Die neue Welt der flüssigen Kristalle und deren Bedeutung für Physik, Chemie, Technik und Biologie. Leipzig 1911. pp. viii + 388. ill. (*Recd.* 22/6/21.)

MICHAELIS, LEONOR. Praktikum der physikalischen Chemie insbesondere der Kolloidchemie für Mediziner und Biologen. Berlin 1921. pp. viii + 160. ill. (*Recd.* 22/6/21.)

MINISTRY OF MUNITIONS and DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH. Technical records of explosives supply 1915—1918. No. 1. Recovery of sulphuric and nitric acids from acids used in the manufacture of explosives: denitration and absorption. London 1920. pp. viii + 56. ill. 12s. 6d. net. (*Recd.* 18/6/21.)

MITSCHERLICH, EDHARD ALFRED. Bodenkunde für Land- und Forstwirte. 3rd edition. Berlin 1920. pp. xii + 355. ill. (*Recd.* 15/7/21.)

NERNST, WALTHER. Theoretische Chemie. 8th—10th edition. Stuttgart 1921. pp. xvi + 896. ill. (*Recd.* 22/6/21.)

OSTWALD, WILHELM. Physikalische Farbenlehre. Leipzig 1919. pp. xii + 259. ill. (*Recd.* 22/6/21.)

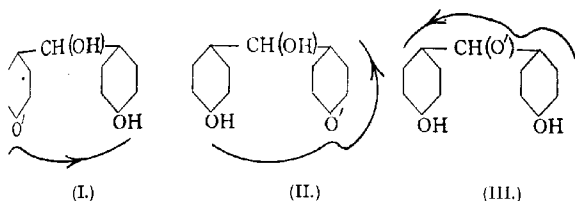
— Die Farbenfel. 4th—5th edition. Leipzig 1920. pp. viii + 45. ill. (*Recd.* 22/6/21.)

PLANCK, MAX. Vorlesungen über Thermodynamik. 6th edition. Berlin 1921. pp. x + 292. (*Recd.* 28/6/21.)

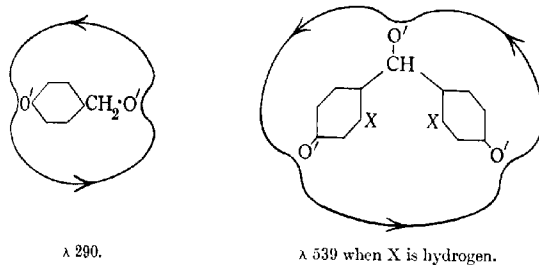
TUNMANN, OTTO. Pflanzenmikrochemie. Berlin 1913. pp. xx + 631. ill. (*Recd.* 6/7/21.)

WASHINGTON, LIBRARY OF CONGRESS. List of references on dyestuffs chemistry, manufacture, trade. Compiled under the direction of Herman H. B. Meyer. Washington 1919. pp. 186. (*Reference.*) 5s. net.

In the dicyclic compounds, the orbit, extending completely round the active part of the molecule, is elliptic and of approximately twice the size; consequently the periodic time is almost double. It is less than double because the attracting mass has been increased, as well as the size of the orbit. Taking *pp'*-dihydroxybenzhydrol as the simplest dicyclic substance, the following diagram approximately represents the motion, with three kinks in the orbit.



The following figures represent my conception of the complete orbits, allowing for the fact that the rings in dihydroxybenzhydrol are most likely inclined to one another at the tetrahedral angle of  $109^\circ$ .



Now, experiment shows that when a dicyclic substance is doubly linked (that is, when the two positions marked X are united by O, NH, S, etc.) the colour becomes lower in a constant proportion for a given linking. Thus :

$$\frac{\lambda_{\text{fluorescein}}}{\lambda_{\text{phenolphthalein}}} = \frac{\lambda_{\text{resorutin}}}{\lambda_{\text{indophenol}}} = 0.89; *$$

this is the value of the factor for the oxo-linking, —O—.

\* I have investigated ten cases of this sort, giving an average of 0.891 for the oxo-linking factor, with very little variation.



I therefore supplement the above conception of the dicyclic orbit with the supposition that a second linking draws the two rings closer together and so contracts the orbit in constant proportion for a given linking, making it more circular and therefore leading to a smaller absorption wave-length.

In general, it may be noted that this orbit theory bears a considerable resemblance to the theories of Hewitt and of Watson and Meek of the three and five tautomerisms, for most of their three-tautomerism substances are "monocyclic," and my "dicyclic" substances can be written so as to exhibit five tautomerisms more frequently than any other number.

#### *Method of Calculating the Colour of Dicyclic Substances.*

This follows immediately from the above theory. Two phenol rings taken together form the "parent-substance" and the constant fundamental absorption wave-length  $\lambda$  1380 is assigned to this combination. This figure is multiplied by the linking-factors of the group or groups joining the rings.

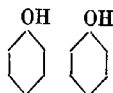
The product is the absorption wave-length of the *prototype* of the coloured substance under consideration, that is, dihydroxybenzhydrol if the linking group is CH $\cdot$ OH, indophenol if the linking group is NOH, resorufin if there are the two linking groups, NOH and O, and so on.

This prototype wave-length is then multiplied by the "colour-factors" corresponding with all the side-groups or inactive rings in the molecule, and the product is the absorption wave-length of the coloured substance.

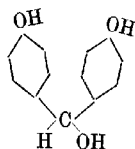
Thus, to calculate the colour of fluorescein,  $\lambda$  1380 is multiplied first by 0.39 ("hydroxymethylene-linking factor"). The product  $\lambda$  539 is the absorption wave-length of *pp'*-dihydroxybenzhydrol. This is then multiplied by 0.891 ("oxo-linking factor"); the product  $\lambda$  480 is the absorption wave-length of 3:6-dihydroxyxanthhydrol, which is the *prototype* of fluorescein. Fluorescein is the *ortho*-benzoic acid derivative of 3:6-dihydroxyxanthhydrol, and the calculation is completed by multiplying  $\lambda$  480 by the benzoic acid colour-factor,\* which, as it represents a "load" outside the orbit, is greater than unity, namely, 1.029. Hence

\* The benzoic acid factor 1.029 may itself be resolved into a phenyl factor (1.026) and an *ortho*-carboxyl factor (1.003). Using the former with  $\lambda$  480 of dihydroxyxanthhydrol, we get the colour of phenyldihydroxyxanthhydrol (resorcinolbenzein) =  $\lambda$  493 as another intermediate stage on the way to fluorescein.

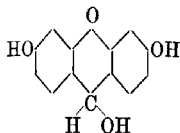
fluorescein has  $\lambda_z = 480 \times 1.029 = 494.5$ . Representing the whole calculation by one equation, we have  $\lambda_z = 1380 \times 0.39 \times 0.891 \times 1.029 = 494.5$ . This agrees with the observed value ( $\lambda 493.5$  to  $494$ ).



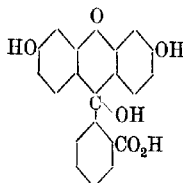
Two phenol rings.  
 $\lambda$  1380.



Dihydroxybenzhydrol.  
Obs.  $\lambda$  539 (calc.  $\lambda$  538).



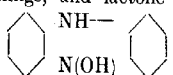
Dihydroxyanthanthrydrol.  
Obs.  $\lambda$  479 (calc.  $\lambda$  480).

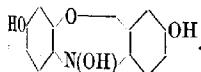


Fluorescein.  
 $\lambda$  494.

The factors may be combined in any order; thus, to calculate the colour of fluorescein, that of phenolphthalein may first be calculated ( $\lambda 1380 \times 0.39 \times 1.029 = \lambda 555$ ) and its wave-length finally multiplied by the oxo-linking factor 0.891.

For the purpose of these calculations it is necessary to write all constitutional formulæ in their most hydroxylated form, eliminating quinonoid bonds, para-linkings, and lactone rings. Thus,

for example, phenazine is written  and resorufin



It is a deduction from such a theory

that the colour of dicyclic substances comes down from the infrared with increasing complexity of linking, not up from the ultraviolet, as is usually supposed. On the other hand, increasing complexity *outside* the linkings puts the colour up again, as is well known.

Returning to the monocyclic coloured substances, I now append table, giving the value of the colour-factors.

*Monocyclic Colour-factors.*

Name of factor.	Property of factor.	Numerical value.
A. Phenyl	$\text{CH}_2\text{OH} \longrightarrow \text{PhCH}_2\text{OH} \longrightarrow \text{Ph}_2\text{C}\cdot\text{OH}$	1.135
B. <i>ortho</i> -Carboxyl	Phenyl compound $\longrightarrow$ phthalein	1.053
C. Phthalein	$\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ introduced into a carbinol	1.200†
D. Amino-	Calculation of aniline derivatives from phenol derivatives	1.140
E. <i>N</i> -methyl	Calculation of methylamino- and dimethylamino-compounds from amino-compounds	1.035
F. Methylamino-	Calculation of methylamino-compounds from hydroxyl compounds	1.180‡
G. Dimethylamino-	Calculation of dimethylamino- from hydroxyl compounds	1.222‡

† This is factor A  $\times$  factor B. Third places of decimals are estimates.

‡ These are D  $\times$  E and D  $\times$  E<sup>2</sup>.

The next table gives the results of applying these factors.

*The Calculated Colours of Monocyclic Substances.*

Name. §	Relation to <i>p</i> -hydroxybenzyl alcohol.	Detailed calculation.	Colour.	
			Calc.	Obs.
1. Fuchson	Two phenyl groups	$\lambda 290 \times (1.135)^2$	$\lambda 374$	$\lambda 380$ (alc.)
2. Fuchson-ionium salts	Two phenyl groups, also $\text{NH}_4^+$ vice OH	$\lambda 290 \times (1.135)^2 \times 1.140$	$\lambda 426$	$\lambda 429$
3. Fuchsonedimethyl-ionium salts	Two phenyl groups, also $\text{NMe}_2$ vice OH	$\lambda 290 \times (1.135)^2 \times 1.222$	$\lambda 457$	$\lambda 455$
4. Hydroxyphenyl-phthalide	Factor C	$\lambda 290 \times 1.20$	$\lambda 348$	$\lambda 350$
5. Hydroxydiphenyl-phthalide	Factors A and C	$\lambda 290 \times 1.135 \times 1.20$	$\lambda 394$	$\lambda 395$
6. Dimethylaminodiphenylphthalide	Factors A, C, and G	$\lambda 290 \times 1.135 \times 1.222 \times 1.20$	$\lambda 483$	$\lambda 480$
7. Dimethylaminobenzhydrol	Factors A and G	$\lambda 290 \times 1.135 \times 1.222$	$\lambda 401$	$\lambda 400$

NOTE.—All the observations recorded in this table (except the first) were made with aqueous solutions in order to get complete ionisation.

§ The formulæ of these compounds are given at the end of the paper.

These constitute about half the possible derivatives of *p*-hydroxybenzyl alcohol; the remaining six have bands in the ultra-violet only, and means for their examination are not at my disposal. I venture, however, to predict their absorption bands, namely,

<i>p</i> -Aminobenzyl alcohol	(weak aqueous acid)	$\lambda 330$
<i>p</i> -Dimethylaminobenzyl alcohol	( " " " )	$\lambda 354$
<i>p</i> -Hydroxybenzhydrol	(weak aqueous alkali)	$\lambda 329$
4-Hydroxyphthalide	( " " " )	$\lambda 307$
<i>p</i> -Aminobenzhydrol	(weak aqueous acid)	$\lambda 375$
4-Aminophthalide	( " " " )	$\lambda 350$

The rough prediction can also be made that the corresponding *ortho*-derivatives, for example, saligenin and *o*-hydroxybenzhydrol, will have bands at about 30 units higher than the *para*-derivatives.

Two future extensions of the theory in respect to monocyclic coloured substances can be pointed out: (1) the active ring may be derived from thiophen, furan, pyrrole, naphthalene, etc., as

well as from benzene, (2) the secondary group need not be  $-\text{CH}_2\text{OH}$ , but by analogy may be  $-\text{NH}\cdot\text{OH}$  (giving the quinoneimine family; hydroxylated form), or  $-\text{O}\cdot\text{OH}$  (giving the quinone family), or  $-\text{S}\cdot\text{OH}$  (giving an unknown group [thioquinone]). It is to be noted that all "monocyclic" colours are yellow or orange ( $\lambda$  less than 500).

Part II. Details of the Calculation of the Colour of Dicyclic Compounds.

For this calculation two tables are required, one giving the linking-factors which contract the orbit, and the other the group colour-factors which expand the orbit.

Table of Linking-factors.

Name.	Numerical value.
A. Methylene	$-\text{CH}_2-$ 0.650*
B. Methenyl	$>\text{CH}-$ 0.645 (for triphenylcarbinol colours)
C. Imino-	$-\text{NH}-$ 0.780*
D. Oxo-	$-\text{O}-$ 0.891
E. Thio-	$-\text{S}-$ 0.920*
F. Hydroxymethylene	$-\text{CH}(\text{OH})-$ 0.390
G. Keto-	$-\text{CO}-$ 0.235
H. Hydroxymethenyl	$>\text{C}(\text{OH})-$ 0.387 (for triphenylcarbinol colours)
I. Oximino-	$-\text{N}(\text{OH})-$ 0.470*
J. Sulphoxide	$-\text{SO}-$ 0.55 (inferred, not experimental)]

\* The third place of decimals is as yet provisional in these cases.

I have worked out about thirty group-colour-factors, of which the most important are given below.†

Table of Dicyclic Group-colour-factors.

1. $\text{NH}_2/\text{OH}$	= 1.007 (used to calculate aniline colours from phenol colours)
2. $\text{NMe}_2/\text{OH}$	= 1.035 ( " " methylaniline " " " )
3. $\text{NMe}_2/\text{OH}$	= 1.059 ( " " dimethylaniline " " " )
4. $\text{NEt}_2/\text{OH}$	= 1.061 ( " " diethylaniline " " " )
5. $\text{NPh}_2/\text{OH}$	= 1.060 ( " " diphenylamine " " " )
6. $\text{NHPb}/\text{NH}_2$	= 1.052 (substitution of Ph for H in an "active" amino-group)
7. $\text{CPh}/\text{CH}$ } $\text{NPh}/\text{NH}$ }	= 1.026 (substitution of Ph for H in any linking group)
8. $\text{C}_6\text{H}_4\text{CO}_2\text{H}/\text{H}$	= 1.029 (used to calculate phthalein and rhodamine colours from those of hydrols)
9. $\text{C}_6\text{H}_4\text{SO}_3\text{H}/\text{H}$	= 1.045 (used to calculate sulphonaphthalein colours from those of hydrols)
10. $\left. \begin{array}{l} \text{ortho-CH}_3 \\ \text{ortho-Et} \\ \text{ortho-Cl} \\ \text{ortho-Br} \end{array} \right\}$	= 1.013 { used for substituents <i>ortho</i> to the active group }
11. <i>meta</i> -Groups	= 1.026 ( " " " <i>meta</i> " " " )

† Most of the remainder are to be found in A., 1921, 120, ii, 6, where  $\text{N-ethyl 1.023}$  should read " $\text{NEt}_2$  1.023." Note should also be taken that the figures in the abstract refer to substitution of a group for hydrogen, whereas in this paper substitution for hydroxyl is the basis of calculation.

It is to be most carefully noted that these factors only apply to the dicyclic group. The monocyclic factors (page 1660) are much larger than these.

*Calculation of the Colour of Familiar Dicyclic Substances.\**

A.—The simplest dicyclic substances are those with only one linking group.

			Obs. (in water), $\lambda$ 539
1. <i>pp'</i> -Dihydroxybenzhydrol contains the linking F.....	$\lambda_x = 1380 \times 0.39$	= 538	
2. Michler's carbinol is the foregoing with $\text{NMe}_2$ for OH (twice) .....	$\lambda_x = 1380 \times 0.39 \times (1.059)^2 = 603$		$\lambda$ 603
3. Michler's ketone is the foregoing with linking G for F .....	$\lambda_x = 1380 \times 0.235 \times (1.059)^2 = 363$		$\lambda$ 364
4. Indophenol contains the linking I .....	$\lambda_x = 1380 \times 0.47$	= 649	$\lambda$ 650
5. Bindschedler's green contains the linking I and two $\text{NMe}_2$ groups .....	$\lambda_x = 1380 \times 0.47 \times (1.059)^2 = 728$		$\lambda$ 730
6. Indamine contains the linking I and two $\text{NH}_2$ groups .....	$\lambda_x = 1380 \times 0.47 \times (1.007)^2 = 658$		$\lambda$ 660

Nearly all the other possible, singly-linked, dicyclic substances will be found on calculation to have colours in the infra-red, for example, dihydroxydiphenylmethane  $\lambda$  897, quinol hemi-ether  $\lambda$  1225, and dihydroxydiphenylamine  $\lambda$  1075.

A few others, like *pp'*-dihydroxybenzophenone (calculated  $\lambda$  324), are coloured in the ultra-violet. I hope that some one will measure the absorption bands of these substances so that it may be ascertained whether the theory still holds in these extreme cases.

B.—The next simplest are prototype, doubly-linked substances, that is, those constituted of only two linking groups and the active rings.

			Obs. (in water), $\lambda$
7. Dihydroxyxanthhydrol has linkings D and F .....	$\lambda_x = 1380 \times 0.39 \times 0.891 = 479$		$\lambda$ 479
8. Dihydroxyacridine has linkings C and F .....	$\lambda_x = 1380 \times 0.39 \times 0.78 = 420$		$\lambda$ 421
9. Dihydroxyphenazine has linkings C and I .....	$\lambda_x = 1380 \times 0.78 \times 0.47 = 506$		$\lambda$ 510
10. 2:7-Dihydroxyanthracene has linkings A and F .....	$\lambda_x = 1380 \times 0.65 \times 0.39 = 350$		$\lambda$ 350
11. Resorufin has linkings D and I .....	$\lambda_x = 1380 \times 0.89 \times 0.47 = 577$		$\lambda$ 576
12. Thionol has linkings E and I .....	$\lambda_x = 1380 \times 0.92 \times 0.47 = 596$		$\lambda$ 595
13. Pyronine is No. 7 with $2\text{NMe}_2$ for 2OH .....	$\lambda_x = 479 \times (1.059)^2 = 537$		$\lambda$ 537
14. Methylene-blue is No. 12 with $2\text{NMe}_2$ for 2OH .....	$\lambda_x = 596 \times (1.059)^2 = 668$		$\lambda$ 667+
15. Ethylene-blue is No. 12 with $2\text{NEt}_2$ for 2OH .....	$\lambda_x = 596 \times (1.061)^2 = 672$		$\lambda$ 673

\* The formulae of these compounds are given at the end of the paper.

† See "Rufol" (Beilstein, "Organische Chemie," II, 999), which has the required colour.

C.—The next simplest are triphenylcarbinol and phenazine dyes which one ring is inactive, namely, the benzeins, phthaleins, bodanimes, "sulphonephthaleins," safranines, benzoflavines, etc.

			Obs. (in water).
6. Benzaurin is the phenyl derivative of No. 1 ...	$\lambda_z = 538 \times 1.026$	$= 553$	$\lambda$ 553
7. Phenolphthalein is the $C_6H_4CO_2H$ derivative of No. 1	$\lambda_z = 538 \times 1.029$	$= 555$	$\lambda$ 554
8. Tetrabromobenzaurin has 4Br all <i>ortho</i> to OH .....	$\lambda_z = 553 \times (1.013)^1$	$= 583$	$\lambda$ 583
9. Malachite-green is the phenyl derivative of No. 2 ...	$\lambda_z = 603 \times 1.026$	$= 619$	$\lambda$ 619
10. Brilliant-green is the tetraethyl derivative .....	$\lambda_z = 619 \div (1.059)^2 \times (1.061)^2$	$= 623$	$\lambda$ 622
11. Rhodamine is the $C_6H_4CO_2H$ derivative of No. 13	$\lambda_z = 537 \times 1.029$	$= 552$	$\lambda$ 553
12. Doebner's violet is No. 16 with $2NH_2$ for $2OH$ .....	$\lambda_z = 553 \times (1.007)^2$	$= 561$	$\lambda$ 562
13. Safranine is phenyldiaminophenazine (see No. 9) .....	$\lambda_z = 506 \times (1.007)^2 \times 1.026$	$= 527$	$\lambda$ 525 + $\lambda$ 505
Benzoflavine is phenyldiaminoscridine (see No. 8) .....	$\lambda_z = 420 \times (1.007)^2 \times 1.026$	$= 437$	$\lambda$ 450*
14. Eosine is No. 17 with the oxo-linking and 4Br	$\lambda_z = 555 \times 0.891 \times (1.013)^1$	$= 521$	$\lambda$ 521
15. Thymolsulphonephthalein is No. 1 with $C_6H_4SO_2H$ , $2CH_3$ ( <i>meta</i> ) and $2C_2H_5$ ( <i>ortho</i> ) ...	$\lambda_z = 538 \times 1.045 \times (1.026)^2 \times (1.013)^2 = 607$		$\lambda$ 604

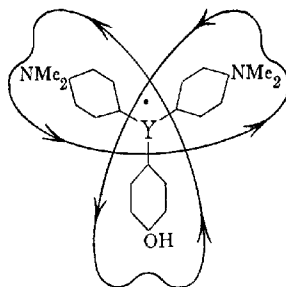
\* Commercial specimen, possibly containing methyl groups.

It is to be noted that the factors can be multiplied and divided actually, giving new factors for special purposes. Thus a special franine factor is obtained by multiplying the  $NH$ , the  $NOH$ , and the  $Ph$  factors together and dividing by the  $PhC(OH)$  factor ( $0.26 \times 0.39$ ). This gives 0.94, by means of which the colour of any safranine can be calculated from that of the corresponding benzaurin.

In this way, for example, the indulines and nigrosines can be correlated with the phenyl dye analogous to malachite-green.

D.—The remaining class has three rings, all of which are active, owing to the attraction of the central carbinol hydroxyl group orbit round the whole molecule is unstable, so that instead of

such an orbit, a looped or trefoil orbit is performed by the moving particle, and only two rings at a time act.



Where  $Y = C(OH)$ .

This assumption is necessary to explain why the three symmetrical substances aurin, pararosaniline, and crystal-violet have colours which are very close to those of dihydroxybenzhydrol, diamminobenzhydrol, and Michler's carbinol.

The factor  $H$  ("hydroxymethylene") of value  $0.387$  is used here:

			Obs. (in water):
27. Aurin: Two phenol rings...	$\lambda_s = 1380 \times 0.387$	$= 534$	$\lambda \ 534$
28. Pararosaniline: Two aniline rings .....	$\lambda_s = 1380 \times (1.007)^2 \times 0.387 = 542$		$\lambda \ 543$
29. Crystal-violet: Two dimethylaniline rings .....	$\lambda_s = 1380 \times (1.059)^2 \times 0.387 = 598$		$\lambda \ 596$
30. Aniline-blue: Two diphenylamine rings .....	$\lambda_s = 1380 \times (1.060)^2 \times 0.387 = 600$		$\lambda \ 594$

Since the hydroxymethylene factor  $F$  is  $0.390$ , the relation to the benzhydrol colours is thus brought out, the orbits being almost identical.

This new theory with respect to substances with *three* active rings requires that such a substance as "*p*-hydroxy-malachite-green" (formula above) shall exhibit two colours simultaneously. This is in accordance with fact. This substance is purple, with  $\lambda \ 578$ , when faintly alkaline, and blue, with  $\lambda \ 608$ , when faintly acid, and shows both bands when neutral; the lower band is close to the position of the band of hydroxydimethylaminobenzhydrol, and the upper band is close to the position of the band of bisdimethylaminobenzhydrol ( $\lambda \ 571$  and  $603$  respectively). Therefore, when the substance is neutral, it has the trefoil orbit and shows both bands; when it is acid, the  $-C_6H_4 \cdot OH$  group is suppressed and the substance has the same orbit as Michler's carbinol; when it

is alkaline, one  $-C_6H_4 \cdot NMe_2$  group is suppressed and the substance behaves almost as if it were hydroxydimethylaminobenzhydrol.

In the same way, the green colour ( $\lambda$  632) of acid crystal-violet is explained: one of the groups is no longer active, but becomes  $-C_6H_4 \cdot NHMe_2Cl$ , the orbit becomes much the same as that of malachite-green, and the colour is that of a "loaded" malachite-green. Finally, if much acid is present, two of the groups become  $-C_6H_4 \cdot NHMe_2Cl$  and the substance then contains only *one* active ring and is monocyclic and yellow (observed  $\lambda$  420). Similarly, acid malachite-green is yellow and is monocyclic (observed  $\lambda$  438).

Other substances, such as oxyhemoglobin and carmin, which exhibit double-banded colours will probably be shown to be capable of similar alternative orbits.

Some notes on the extension of the theory are now appended.

1. As a rule, the position of the absorption band is very slightly affected if the active groups are not in the *para*-position with respect to the linking group. Taking  $\lambda$  1380 as the value of two *p*-hydroxyphenyl rings, the value for two *m*-hydroxyphenyl rings lies between  $\lambda$  1385 and  $\lambda$  1390, and the value for one *para*- with one *ortho*-ring is about  $\lambda$  1395. An example of the former is quinolphthalein, which is isomeric with fluorescein but has the hydroxyl groups in the *meta*-position with respect to the linking hydroxymethenyl group and has  $\lambda$  499 (with a faint *blue* fluorescence) in sodium hydroxide solution and rather lower in ammonia.\* An example of the *ortho-para*-grouping is phenol-*p*-cresolphthalein, which has  $\lambda$  572, whilst phenol-*o*-cresolphthalein (which is a *pp'*-compound) has  $\lambda$  562.

2. The calculation of the colour of naphthol and naphthylamine dyes gives irregular results, but I am of opinion that this is the fault, not of the theory, but of the constitutions assigned to the defaulting substances, one of which, for example, has recently been shown to be an *oo'*- instead of a *pp'*-compound.† The naphthol/phenol factor is in any case very high, varying between 1.08 and 1.14.

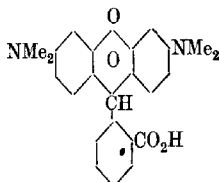
3. The factors of linking groups containing oxygen, such as  $CH \cdot OH$ ,  $NOH$ , are related to those of the corresponding non-oxygenated groups by the fraction  $\frac{2}{3}$ . This probably represents an undiscovered law of nature in connexion with electron movements. The number of fundamental factors can thus be reduced to four, namely, those corresponding with  $CH_2$ ,  $NH$ ,  $O$ , and  $S$ , and the formula of any coloured compound is therefore most simply written, for the purpose of this paper, as that of its leuco-compound

\* Fluorescein has  $\lambda$  494.

†  $\alpha$ -Naphtholphthalein (*Ber.*, 1920, 53, [B], 1445).



with the addition of an unbound oxygen atom, the value of the



latter being counted as  $\frac{2}{3}$  in the calculation; for example, rhodamine: two dimethylaniline rings =  $\lambda 1380 \times (1.059)^2 = \lambda 1547$ ; the  $\cdot\text{O}\cdot$  and  $\cdot\text{CH}_2\cdot$  linkings lead to multiplying by 0.891 and by 0.65, giving  $\lambda 896$ . This is then multiplied by the benzoic factor and by  $\frac{2}{3}$ , giving  $\lambda 896 \times 1.029 \times 0.6 = \lambda 552$  (see No. 21).

It does not necessarily follow, however, that the leuco-compounds themselves possess sharp absorption bands.

*Possible New Classes of Coloured Substances.*

(1) Dihydroxydihydroanthracene gives  $\lambda 583$  by the theory, but as it is a leuco-compound it may not be capable of exhibiting this colour.

(2) Quinol-ether oxide,  $\text{O}:\langle\text{C}_6\text{H}_4\rangle:\text{O}:\langle\text{C}_6\text{H}_4\rangle:\text{O}$ , should have  $\lambda 735$

and may possibly exist as a (green) salt,  $\text{O}:\langle\text{C}_6\text{H}_4\rangle:\text{OCl}:\langle\text{C}_6\text{H}_4\rangle:\text{OH}^*$

The existence of similar compounds with S and S'O as the linking groups is possible, and also of isomerides with *m*-hydroxyl groups (resorcinol-ether oxide, etc.).

(3) The compound also gives a calculated colour ( $\lambda 702$ ) lying within the visible spectrum.

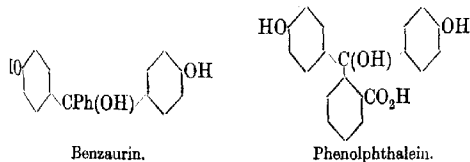
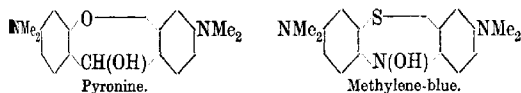
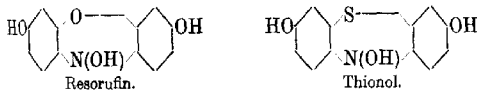
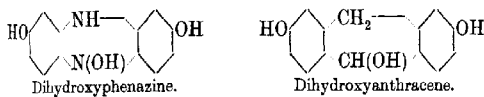
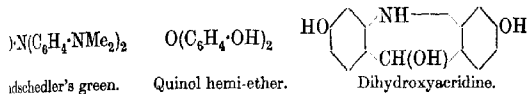
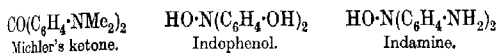
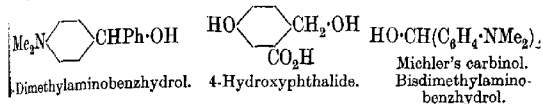
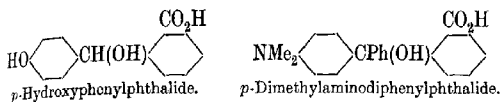
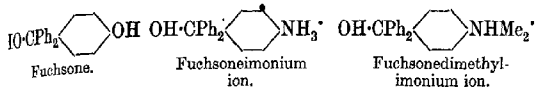
(4) 2:7- (instead of 3:6-) Isomerides of the oxazine, acridine, and thiazine dyes appear to be unknown, but it is to be expected that they would be valuable dyes with slightly higher colours than the 3:6-isomerides and would exhibit scarcely any fluorescence.

*The Two Exceptions.*—(a) 3:6-Dihydroxyxanthone is described as having  $\lambda 381$  (E. R. Watson, "Colour and Chemical Constitution," p. 88), whereas the theory gives  $\lambda 288$ . It is possible that the colour was observed in the absence of alkali, in which case the result would be abnormal, as in the case of phenol, the spectrum of which is different from that of the phenoxide ion.

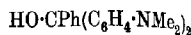
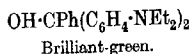
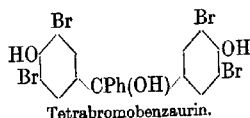
\* Compare quinhidrone as  $\text{O}:\langle\text{C}_6\text{H}_4\rangle:\text{O}(\text{OH})\langle\text{C}_6\text{H}_4\rangle:\text{OH}$ .

(b) 2:7-Dihydroxyanthraquinone has a high colour, whereas the theory predicts a value of  $\lambda$  smaller than 100. Probably, when two carbonyl groups are present, they co-operate in producing a special vibration quite different from that produced by one carbonyl group.

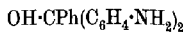
(hydroxylated Formulae of the Substances dealt with in the Paper (excepting those given in the text).



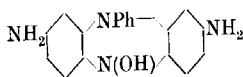
1668 CALCULATION OF COLOUR OF "CYCLIC" COLOURED SUBSTANCES.



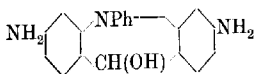
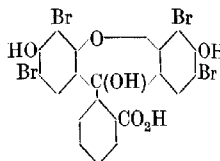
Malachite-green.



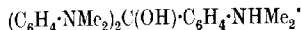
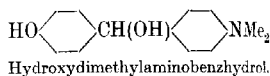
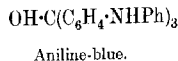
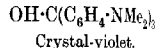
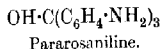
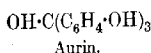
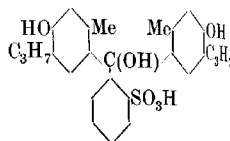
Döbner's violet.



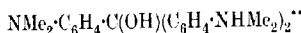
Safranine.  
(or with NPh and NOH reversed.)



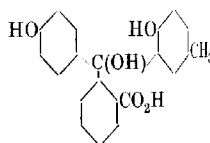
Benzoflavine.



Crystal-violet ion (green) in moderately acid solution.



Crystal-violet ion (yellow) in strongly acid solution.



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CLXXXIX.—*The Hydration of the Fibres of Soap Curd.*  
*Part III. Sorption by Sodium Palmitate.*

By MARY EVELYN LAING.

PREVIOUS work (McBain and Taylor, T., 1919, **115**, 1300; McBain and Martin, this vol., p. 1369; McBain and Salmon, *ibid.*, p. 1374) has shown that the fibres which form the structural basis of soap curd abstract by their hydration definite amounts of water from the solution with which they are in contact and thus give rise to the appearance of negative sorption of the salts dissolved in the lye or mother-liquor. The value  $\text{NaP}, 2.1\text{H}_2\text{O}$  for the hydration of sodium palmitate in the presence of a nearly saturated solution of sodium chloride at  $90^\circ$  has been established by several methods. It has been shown that these fibres sorb small amounts of sodium chloride, and the same has been found to be true of sodium sulphate, except in the presence of a large amount of some other salt.

The present work was undertaken in the hope of finding some easily analysable reference substance which would be applicable in all cases to the determination of the hydration of soap fibres and incidentally to the extension of the existing scanty knowledge of the sorption of various substances by curd fibres.

Glycerol is the only one of the substances here investigated which is neither appreciably sorbed nor decomposed by the soap; it is not, however, easy to use as a reference substance. This result is of twofold interest. In the first place, the hydration value obtained with it,  $\text{NaP}, 2.0\text{H}_2\text{O}$ , agrees with the value obtained by the previous methods. In the second place, glycerol being a most important material from a commercial point of view, it becomes evident that the loss of the glycerol retained in the soap (equal, perhaps, to 10 per cent. of the world's output) is not inherently unavoidable, for all the glycerol may be washed out from the soap curd, being not chemically combined, but merely held in the mechanically entangled lye. The problem is that of washing a wet precipitate. The expense of recovering a large part of this glycerol is a commercial question, but it is possible to do it by a suitable modification of the process of soap-boiling.

## EXPERIMENTAL.

Pure sodium palmitate was prepared as follows: Sodium wire which had been cleaned in methylated ether was dissolved in

alcohol that had been distilled after standing for a year over calcium oxide and was therefore thoroughly dry. The sodium ethoxide formed was treated with palmitic acid (Kahlbaum) until the alcoholic soap solution, after dilution with a recently boiled mixture of alcohol and water (3 : 1), was found, by repeated tests, to give a neutral reaction with a neutral alcoholic solution of phenolphthalein. After being isolated, the sodium palmitate was dried for a week in a vacuum desiccator and was thus obtained as a pure white powder.

The dry, neutral sodium palmitate was weighed into a glass tube and dissolved in the necessary quantity of a solution of sodium chloride containing the reference substance to make the solution approximately normal with respect to sodium palmitate. Glass was not affected by sodium chloride, but it was not used with alkali, because in blank experiments the concentration of  $N/10$  sodium hydroxide increased by 5 per cent. and of a  $2.5N$  solution by 11 per cent. after shaking at  $90^\circ$  during one week.

The glass tubes were sealed and shaken for one week at  $90^\circ$  and allowed to stand for another week at  $90^\circ$ . In this way a maximum amount of lye was obtained, as in some cases the separation of the two layers required several days and in others there was no appreciable separation after long periods at  $90^\circ$ . The tubes were opened and the lye was withdrawn with a pipette fitted with a glass filter-cap specially designed to filter all the solution through a single thickness of filter-paper about 1 mm. in diameter. The first few drops of lye were discarded in case the tiny piece of filter-paper had sorbed any of the reference substance. In all later analyses the water content of the lye was found by evaporation of samples, after a few drops of hydrochloric acid had been added to decompose any soap that might possibly have been present. All duplicate samples gave the same percentage loss of water.

In some cases the concentration of the reference substance was very low owing to the fact that some salts were salted out in concentrated sodium chloride solution, their solubility being lessened. In such cases the blank analyses (in duplicate) were alone taken to give the original concentration. In others the weighed amounts taken agreed with those analytically determined in blank experiments.

It should be clearly understood that the absence of glycerol from curd fibres which have been salted out at  $90^\circ$  has nothing at all to do with the phenomena evolved when "neat soap" is formed as an upper layer in soap-boiling. This neat soap containing 30 per cent. of water is not a curd, but it is a liquid, whether gel or sol, and the concentration of glycerol in this liquid is governed

by the law of distribution between it and the lower layer, whether curd or lye. These relationships will be dealt with in other communications from this laboratory.

The previous paragraph therefore refers only to curd in the presence of graining lyes.

All the chemicals employed, except sodium formate, were Kahlbaum's best. All vessels were carefully calibrated. Concentrations are expressed in weight normality, mols. per 1000 grams of water.

#### *Analytical Methods.*

It must always be remembered in evaluating these results that each case represents small differences between large numbers, hence any slight error in the analysis is considerably magnified (up to thirty-fold) in the sorption or hydration results deduced. When the quantity of lye obtained was larger, the results were more accurate, and thus agreed very closely in blank experiments, but duplicate estimations did not give very concordant values when, as in most cases, the quantity of lye was scarcely adequate.

The presence even of traces of an unsaturated acid or of an oxidisable impurity in the soap would prohibit the use of an oxidising material as reference substance.

In most cases, volumetric methods were employed in the preliminary experiments, but where a compound seemed to be a promising reference substance, gravimetric analysis was carried out also.

Glycerol was analysed by the acetin method with the following modifications. The sodium chloride solution or lye containing the glycerol was treated with sulphuric acid to decompose any soap present and the sulphuric acid removed by barium chloride. The ethereal extract of the dried barium residue was evaporated to dryness in a silica flask on a water-bath with the aid of a suction-pump. As any estimation in the presence of a slight trace of water or alcohol was valueless, the residue, before being analysed, was left over-night in a vacuum desiccator containing calcium chloride. The silica flask was fitted with a ground-in silica condenser. This arrangement greatly simplifies the procedure, for with continued boiling in glass the mixture of acetic anhydride and glycerol extract is liable to cake, causing fracture of the flask by local overheating. It also allows of rapid cooling of the contents of the flask.

#### *Experimental Results.*

Incidental observations were made on the characteristics of the soap curd, particularly as regards its hardness and the extent to

which the lye was retained enmeshed in the curd on standing as well as after suction (Table I). For instance, the striking combination of effects produced by small quantities of phenol would be of practical importance were it not for the fact that they are observed only with chemically pure palmitate. Commercial palmitates do not show this behaviour, probably because the effect is, as other experiments show, in the opposite direction with unsaturated soaps such as the oleate. Sodium phenoxide greatly lowers the so-called melting point of curds of pure sodium oleate, an effect which is in the opposite direction to that observed with eight other salts investigated.

TABLE I.

Appearance of the curd and the lye when sodium palmitate is salted out by saturated sodium chloride solution in presence of small amounts of various substances.

Reference substance.	Clear lye visible.	Proportion of the lye finally recovered.*	Curd.
Sodium oxalate	None	$\frac{1}{4}$	—†
Potassium iodide	Scanty	$\frac{1}{10}$	Soft
" bromate	Scanty	$\frac{1}{8}$	—
" chromate	Scanty, pale yellow	$\frac{3}{8}$	Very yellow
Sodium formate	None	$\frac{1}{8}$	Hard
Acetone	Plenty	$\frac{1}{4}$	Very soft
Phenol	None	$\frac{1}{20}$	Very firm
Sodium thiosulphate	Very little	$\frac{1}{4}$	Soft
Glycerol	Scanty	$\frac{1}{4}$	—
Sodium hydroxide	Plenty	$\frac{1}{4}$	Soft

\* See columns 5 and 6 in Tables II and III, which show approximately how much lye was mechanically retained in the curd after suction. The amount of lye obtained was, in most cases, greater than that recorded in column 5, the remainder having been used for the estimation of the water.

† The dash (—) indicates that the appearance and the hardness of the curd were not noticeably different from those of the curd obtained in the absence of the reference substance.

Table II contains the data for nine reference substances (for clearness, the weights are only recorded in rounded-off numbers).

Table III contains the data for the sorption of the reference substances of Table II. The calculation of these results involves the hydration value  $\text{NaP} \cdot 2.1\text{H}_2\text{O}$  previously established, which necessitates a correction of the percentage change in the concentration of the lye recorded in Table II in order to allow for the water abstracted to form the fibres. The true sorption of the reference substance is expressed in three different ways: first, in

TABLE II.

Concentration changes in the added reference substance when sodium palmitate is salted out at 90°.

Reference substance.	Nor-mality of NaP.	Weight nor-mality of reference substance.	Grams used.		Lye obtained.		Percentage change in concentration of reference substance in the lye.
			NaP.	Lye.	Grams.	Nor-mality.	
sodium oxalate	1.0	0.003	5	16	3.8	0.00295	- 17.2
	1.23	0.080	5	20	1.4	0.069	- 13.4
	1.23	0.815	5	20	1.6	0.072	- 11.5
" bromate	0.98	0.080	3	15	2.2	0.071	- 11.3
	1.50	0.0296	5	16	1.9	0.070	- 11.7
	1.50	0.0254	5	16	5	0.0089	- 65.0?
chromate	1.23	0.1962	5	20	4.3	*	*
	0.62	0.1205	3	24	2.6		
formate	0.62	0.1205	3	24	4.8	0.0099	- 17.0
	1.29	0.0649	5	19	2.0	0.095	- 17.4
thiosulphate	1.29	0.0649	5	19	4.1	0.064	- 1.5
	1.25	0.0851	5	19.5	3.6	0.062	- 4.6
mel	0.998	0.0557	4	19.5	0.40	0.069	- 23
	1.10	0.1018	4	17	0.85	0.074	- 16
	0.52	0.1021	3	18	2.6	0.040	- 28
percol	1.10	0.1018	4	17	6.6	0.1059	- 3.6
	0.52	0.1021	3	18	6.8	0.1053	- 3.2

\* The trace of soap in the lye was sufficient to vitiate the analyses, probably owing to the boiling with alkali and permanganate.

percentage of the total reference substance present which has been sorbed by the curd fibres; secondly, in the percentage by weight, that is, the weight in grams sorbed by 100 grams of  $\text{C}_{18}\text{H}_{35}\text{O}_2$ ; thirdly, in order to render the results roughly comparable, in mols. of reference substance sorbed by 1 mol. of sodium palmitate—for an accurate comparison the sorption law would have to be determined for each case.

It should be noted that whereas there is a real positive sorption of the reference substance in each case except glycerol, nevertheless the greater part of the reference substance is left in the lye, and that it forms only an inconsiderable percentage of the weight of the curd fibres themselves.

Other glycerol results, which are not quoted in the tables owing to the inadequate quantities of lye available, always showed a similar increase in concentration of glycerol, in agreement with the fact that it is not sorbed by curd fibres.



TABLE III.

Sorption of various substances by sodium palmitate at 90° in presence of saturated sodium chloride solution.

Reference substance.	Grams of reference substance per 100 grams of water.	Mols. of NaP.	Fate of reference substance.	True sorption of reference substance.		
				Pro-portion per cent.	Percent- age by weight of soap.	Mols. sorbed per 1 mol. of NaP.
Sodium oxalate	0.046	1.0	sorbed	22.63	0.042	0.0608
Potassium iodide	1.322	1.23	"	17.2	0.695	0.012
	1.325	1.23	"	16.1	0.639	0.011
	1.173	0.98	"	11.6	0.561	0.009
	1.168	0.98	"	11.9	0.580	0.010
" bromate	0.494	1.50	reduced	bromide only present		
	0.493	1.50	"	66.8	0.830	0.012
Acetone	0.726	0.615	sorbed	19.0	0.797	0.038
	0.726	0.615	"	19.4	0.811	0.039
Sodium thiosulphate	0.672	1.29	"	5.95	0.177	0.003
	0.672	"	"	9.02	0.177	0.005
Phenol	0.800	1.25	"	21.7	0.401	0.015
	0.800	"	"	11.4	0.303	0.012
	0.524	0.998	"	30.8	0.600	0.018
Glycerol	0.94	1.10	unchanged			
	0.94	0.82	"			

#### *Sorption of Sodium Hydroxide.*

There is an inherent difficulty in experimenting with sodium hydroxide in that it is one of the constituents of the soap itself and it is difficult to be quite sure, first, that the reaction between sodium hydroxide and palmitic acid is completed, because of the salting-out action of saturated sodium chloride solution, and secondly, that the actual hydrolysis of the soap itself has not been altered in the process of salting-out.

The concentrations taken were very low, since for solution between 1.5*N* and 3.0*N* conclusive work had already been carried out (Part I, *loc. cit.*). In that work, repeated experiments showed that concentrated solutions increase in concentration owing to removal of water for the hydration of the curd.

The results in Table IV were obtained by experiments carried out in sealed silver tubes. The solution of sodium palmitate was made up in two ways, namely, in that already recorded and by mixing the requisite quantities of palmitic acid and solution of sodium hydroxide. The last six lines of the table refer to solution of sodium hydroxide which had been directly standardised against the pure palmitic acid used, to ensure that the alterations of concentration of sodium hydroxide were not due to relative

light inaccuracy in making up the comparatively large amounts of sodium palmitate. In all the latter cases, pure ignited sodium chloride in solid form was added to the original charge.

TABLE IV.

Sorption of dilute sodium hydroxide by curd fibres of sodium almitate salted out at 90° by nearly saturated sodium chloride solution.

Preparation.	Weight normality of soap.	Weight normality of excess of NaOH.		Apparent per cent. change.	Mols. of NaOH per 1 mol. of NaP.
		Before.	After.		
aP + brine + excess of NaOH	1.00	0.1163	(a) 0.1029 *	9.5	0.012
			(b) 0.1062		
	1.045	0.1571	(a) 0.1409	9.4	0.015
			(b) 0.1428		
	0.99	0.0993	(a) 0.08136	18.1	0.018
			(b) 0.08140		
HP + brine containing NaOH	0.9618	0.0944	(a) 0.08242	13.4	0.012
			(b) 0.08180		
	1.00	0.2006	(a) 0.0719	14.3	0.29
Standardised HP + NaOH + solid sodium chloride	1.00	0.2081	(a) 0.1856	10.5	0.022
			(b) 0.1869		
	0.9863	0.1120	(a) 0.0820	29.0	0.033
			(b) 0.0768		
	0.9868	0.1163	(a) 0.08275	28.2	0.033
			(b) 0.08433		

\* (a)—(b) refer to experiments in two separate silver tubes, each determined in duplicate.

† In the last series, repeated some months after the first two, the palmitic acid was standardised against the sodium hydroxide employed.

The results show conclusively that there is a real positive sorption of sodium hydroxide from dilute solutions. For 0.1N-sodium hydroxide this amounts to between 10—29 (weighted mean 22 per cent.), and for 0.2N-sodium hydroxide, 10—14 (weighted mean 11 per cent.). The corresponding empirical formula for the curd fibres in both cases is  $\text{NaP}, 2.1\text{H}_2\text{O}, 0.022\text{NaOH}$ .

Although it is improbable that the sorption of sodium hydroxide does not increase at all with concentration, yet the data strongly indicate that this is approximately the case. This is in accordance with results obtained in Part I with concentrated solutions, where pronounced negative sorption was actually observed, so that the amount of water taken up wholly masked the slight amount of sorbed sodium hydroxide. The effect of this would be to bear out what has been emphasised in Parts I and II. The method of

negative sorption yields minimum values, which could be increased, for example, in the case of 3.0*N*-sodium hydroxide, by about 0.4 mol. of water giving a result of, say,  $\text{NaP}, 3.6\text{H}_2\text{O}$  in place of  $\text{NaP}, 3.2\text{H}_2\text{O}$ .

In connexion with other work, it is important to note that the presence of *N*/10-sodium hydroxide has now been proved, not only to eliminate hydrolysis completely, but even to render the curd fibres very slightly alkaline when salted out with concentrated sodium chloride solution.

### *Summary.*

The sorption of widely different substances by soap curd has been investigated for the first time.

When 1 mol. of sodium palmitate is treated with brine containing about 1000 grams of water, 330 grams of sodium chloride, and 5–10 grams of the substance under investigation, an appreciable fraction ( $\frac{1}{10}$  to  $\frac{1}{3}$ ) of the following are sorbed by the soap curd; acetone, phenol, potassium chromate and iodide, sodium acetate, thiosulphate, and hydroxide.

Sodium sulphate and glycerol are quantitatively left in the lye; their apparent presence in soap curd is due only to the enmeshed lye. This solves an old and important problem as to the form in which glycerol is present in soaps.

Under the above conditions (salting out with saturated sodium chloride solution), in confirmation of previous work from this laboratory, the hydration of the solid part of wet soap curd amounts to  $1\text{NaP}, 2\text{H}_2\text{O}$ .

Sodium hydroxide is sorbed by curd fibres to an extent probably not exceeding about 0.02 equivalents of sodium hydroxide to 1 equivalent of sodium palmitate.

In conclusion, I wish to thank the Colston Research Society of the University of Bristol and the Chemical Society for grants for the purchase of pure materials, which enabled this investigation to be carried out.

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CXC.—*The Propagation of Flame in Mixtures of Ethylene and Air.*

By WILLIAM RONALD CHAPMAN.

THE "uniform movement" of flame, which occurs when an inflammable mixture contained in a tube closed at one end is ignited at the open end, affords means of comparison between one inflammable gas and another as regards their general behaviour on burning. The speed of the uniform movement is dependent on the character of the combustible gas and the composition of the mixture that is flamed, but it is also dependent on the experimental conditions, notably on the diameter of the tube in which the mixture is contained. When desirous of comparing one mixture with another, a series of mixtures of one inflammable gas and air with that of another inflammable gas, it is essential, therefore, that the records of speeds employed should have been obtained under standard conditions.

Records of the speed of the uniform movement of flame in all air mixtures with air over the range of inflammability are available for most of the common inflammable gases, as determined in horizontal glass tubes 2.5 cm. in diameter. Thus, for hydrogen reference can be made to Haward and Otagawa (T., 1916, **109**, 83), for methane and acetylene to Mason and Wheeler (T., 1917, **111**, 644; 1919, **115**, 578), and for ethane and the higher paraffins, and for carbon monoxide, to Payman (T., 1919, **115**, 1446, 1454). For ethylene information has not hitherto been available and, since ethylene is an important constituent of coal-gas, it is desirable that it should be.

The present paper records for ethylene (1) its limits of inflammability, and (2) the speed of the uniform movement of flame in all its mixtures with air, as determined in a glass tube 2.5 cm. in diameter.

*Limits of Inflammability.*

The results obtained are given in the table that follows. With gases of larger diameter the limits would, no doubt, be slightly lower (in this connexion see T., 1918, **113**, 656).

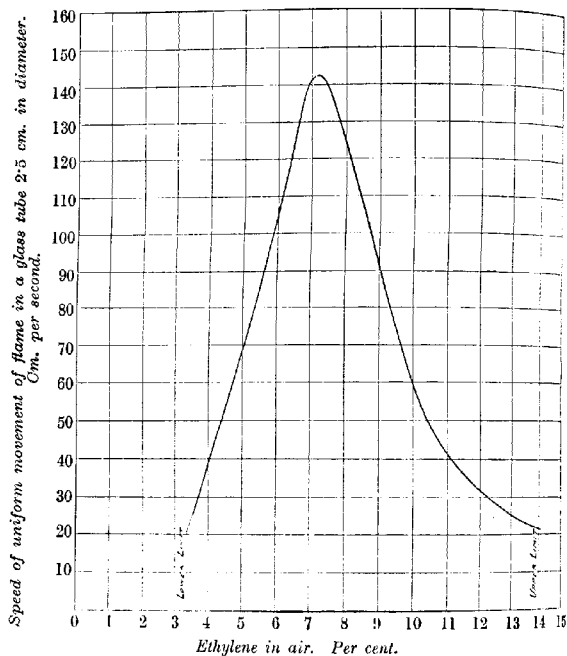
	Ethylene per cent.	Remarks.
Horizontal propagation.		
Lower limit . . . . .	3.4	{ A pale blue flame occupied the upper portion of the tube only. The upper limit flame was tinged with yellow.
Upper limit . . . . .	14.1	

	Ethylene per cent.	Remarks.
Vertical propagation, downward.		
Lower limit .....	3.6	Pale blue disc.
Upper limit .....	13.7	Pale blue, voluminous flame.
Vertical propagation, upward.		
Lower limit .....	3.3	Blue flare of flame.
Upper limit .....	25.6	Smoky, yellow flame, carbon deposited on sides of tube.

### *Speed of Propagation of Flame.*

The measurements of the speed of the uniform movement are most conveniently displayed in diagrammatic form (Fig. 1). The

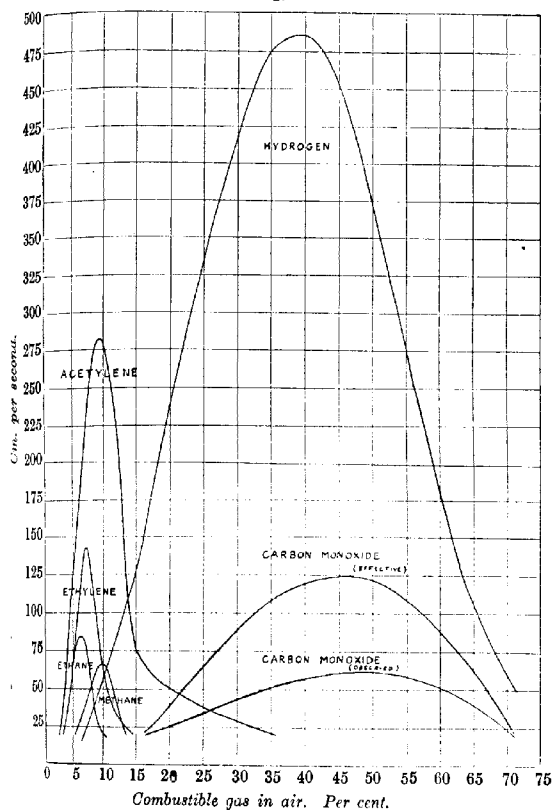
FIG. 1.



curve relating speeds with percentages of ethylene is of a form similar to that obtained with other hydrocarbons; that is to say, the speed of the flame increases rapidly as the percentage of ethylene

increased from that in the lower-limit mixture until a maximum is reached, after which it decreases. As with each of the paraffin hydrocarbons under the same conditions of experiment, the speed of the flame at the limits tends towards a value of 20 cm.

FIG. 2.



per second, which would therefore appear to be a constant for the hydrocarbons.\*

\* With mixtures of carbon monoxide and air the speed of flame at the limits (under the same conditions of experiment) is also about 20 cm. per second; whereas with the lower-limit mixture of hydrogen and air the speed is abnormally slow, namely, 10 cm. per second (see T., 1919, 115, 1444).

In Fig. 2 the speed-percentage curves for the uniform movement of flame in mixtures of air with hydrogen, carbon monoxide (the "effective" values and those "observed" when saturated with water-vapour at 12° and 750 mm.), methane, ethane, acetylene, and ethylene respectively, as determined in horizontal glass tubes 2.5 cm. in diameter, are plotted to the same scale for comparison. The curve for ethylene is intermediate in character between those for methane and acetylene, not only as regards its maximum range, but also in respect of the manner in which it flattens as the upper limit is approached. This flattening of the curve towards the upper limit is just noticeable with methane (it becomes more pronounced when tubes of larger diameter than 2.5 cm. are employed), is quite distinct with ethylene, and is very marked with acetylene, where it is due to exothermic decomposition of excess of the gas (see T. 1919, 115, 578). With ethylene, as with the paraffin hydrocarbons the flattening of the curve as the excess of combustible gas becomes greater is probably due to the liberation of hydrogen at an intermediate stage in the combustion of the hydrocarbon.

The mixture of ethylene and air that contains ethylene and oxygen in combining proportions to form carbon dioxide and steam contains 6.5 per cent. of ethylene, and this mixture has the maximum calorific effect. The maximum speed of uniform movement of flame is, however, obtained with mixtures containing between 7 and 7.25 per cent. of ethylene. This "displacement" of the maximum-speed mixture, which has been observed to a greater or less extent with all mixtures of inflammable gases with air, has been shown by Payman to be an effect of mass action (T., 1920, 117, 48).

Given data respecting the compositions of the maximum-speed mixtures with air of individual combustible gases, and the speeds of flame in them, it is possible to calculate the maximum-speed mixture, and the speed obtainable, when a composite gas, such as coal-gas, containing the individuals in known proportions, is mixed with air. Taking as an example a coal-gas containing

Carbon dioxide	2.6
Ethylene	3.0
Carbon monoxide	14.1
Hydrogen	46.9
Methane	19.0
Ethane	4.5
Nitrogen	9.9

the composition of the maximum-speed mixture can be calculated by means of the formula

$$M = 100 / \left\{ \frac{a}{M_a} + \frac{b}{M_b} + \frac{c}{M_c} + \dots \right\}$$

in which  $a, b, c, \dots$  are the percentages of the individual gases in the coal-gas, and  $M_a, M_b, M_c, \dots$  the percentages in their respective maximum-speed mixtures with air. The result of the calculation is 22.2, meaning that the maximum speed of uniform movement of flame in a tube 2.5 cm. in diameter is obtained when 22.2 per cent. of the coal-gas is present in the mixture with air.

The value of the speed of flame in this mixture can be calculated from the formula

$$S = \frac{l_{S_1} + m_{S_m} + n_{S_n} + \dots}{l + m + n + \dots}$$

in which  $l, m, n, \dots$  are the amounts present of the maximum-speed mixture with air of each constituent gas, and  $S_1, S_m, S_n, \dots$  are the speeds of flame in those mixtures. In the instance given, the calculated speed (using the "effective" value for carbon monoxide) is 210.5 cm. per second.

So far as calculations for different compositions of coal-gas are concerned, a sufficiently close approximation can be obtained by grouping together the paraffins and olefins and treating them as though they were methane. Thus, for the sample of coal-gas taken as an illustration, the maximum-speed mixture calculated on this assumption contains 22.7 per cent. of coal-gas and the speed of flame in that mixture is 206.2 cm. per second.

This research has been extended to include the study of the propagation of flame in mixtures of the higher members of the olefine series of hydrocarbons with air. For propylene, for example, the limits of inflammability (horizontal propagation of flame) are 2.6 and 7.4, and the maximum speed of the uniform movement, under the same conditions of experiment as for ethylene, is 90 cm. per second, obtained with mixtures containing between 4.8 and 5.3 per cent. of propylene. The significance of a comparison between the values obtained for ethylene, propylene, and butylene on the one hand and ethane, propane, and butane on the other will be discussed in a future communication. For the present it may be mentioned that the higher olefins correspond more closely to the paraffins than does ethylene, so far as the speed of uniform movement of flame in their mixtures with air is concerned. Coal-gas contains, in addition to ethylene, appreciable quantities of propylene and butylene, which are usually recorded in analyses as ethylene (or as "olefins"), so that the grouping together of paraffins and olefins when making such calculations as are described above would, in the majority of instances, cause even less departure from an exact calculation than appears in the illustration that is given.



## EXPERIMENTAL.

Ethylene was prepared by the dehydration of absolute ethyl alcohol by phosphoric acid at  $200-220^{\circ}$  (Newth, T., 1901, **79**, 901) and purified by passing through a condenser cooled by solid carbon dioxide. Explosion analysis gave a ratio  $C/A$  of 1.00, showing a high degree of purity. The mixtures with air were prepared over glycerol and water in glass gas-holders and were analysed before use.

The determinations of the limits of inflammability were made in a glass tube 2.5 cm. in diameter and 150 cm. long. The measurements of speeds of flame were made by the "screen-wire" method described by Wheeler (T., 1914, **105**, 2609), a glass tube 2.5 cm. in diameter and 300 cm. long being employed. Three screen-wires were used 25 cm. apart, the first being 20 cm. from the point of ignition. These wires were supported on platinum leads which passed through ground-glass stoppers fitted into tubulures. The tube, which had a tap fused on at one end and could be temporarily closed at the other end by a ground-glass cover, was exhausted of air before each experiment, filled with the required mixture from the gas-holder, re-exhausted and filled again. Ignition in the majority of the experiments was by means of an electric spark at platinum electrodes fused through the walls of the tube 2 cm. from the open end; in the remaining experiments a lighted taper was passed across the mouth of the tube.

The flames were of a pale blue colour tinged with pink. They usually travelled at a uniform speed over a distance of about 90 cm. from the point of ignition; occasionally, with the fastest flames, the "vibratory movement" began before the third screen-wire was reached (70 cm. from the point of ignition), when the measurements of speed between the first and second screen-wires only were recorded. Details of the results are as follow :

Ethylene per cent.	Speed in cm. per sec.	Ethylene per cent.	Speed in cm. per sec.
3.55	25.8	7.20	142.4
3.60	29.4	7.40	138.7
3.80	36.8	7.70	127.5
4.00	41.3	8.10	120.6
4.70	57.9	8.45	113.7
5.40	79.4	8.65	113.4
6.10	108.4	9.00	89.5
6.40	121.6	9.45	72.6
6.45	129.3	10.65	45.5
6.50	129.9	13.35	23.5
6.60	133.5	13.80	22.3
6.90	140.2	14.00	22.2

This work, in which I have been assisted by Mr. C. A. Naylor, has been carried out at the Mines Department Experimental Station, Eskmeals, under the direction of Dr. R. V. Wheeler.

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### *XCI.—The Effect of Temperature on Platinum Black and other Finely-Divided Metals.*

By ROBERT WRIGHT and ROBERT CHRISTIE SMITH.

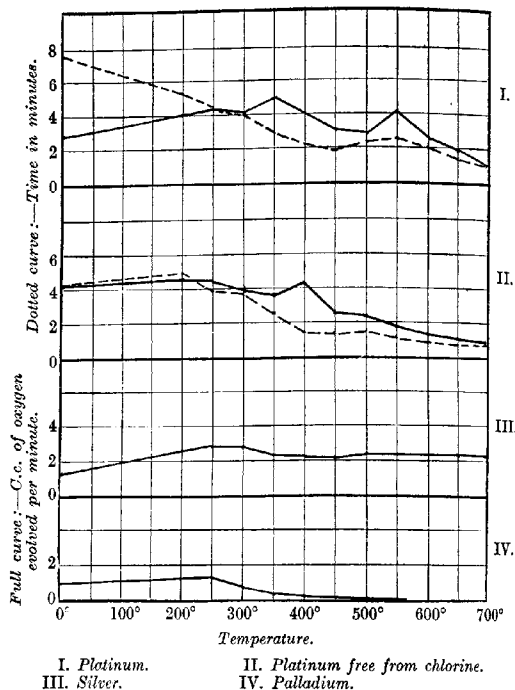
WHEN a freshly-coated platinum plate has been heated to a temperature somewhat above red heat and allowed to cool, the original velvet-black surface becomes grey, the extent of the colour lightening depending on the temperature and the duration of the heating.

This change in platinum black is not attended by any alteration in weight, and cannot therefore be due to oxidation or to the removal of the deposited surface. Moreover, the change does not take place at any definite temperature, as a plate heated in a resistance furnace and examined at every 50° began to show the change at 300°, the effect increasing with rise of temperature until, at 900°, the deposit had become almost white.

In order to determine whether the heating produced any other change in the platinum black beyond the alteration of colour, several properties of the metal were examined, measurements being made immediately after the deposition of a fresh coat and also after heating the coated plate to a series of definite temperatures. The properties which gave most satisfactory results were the decomposition of hydrogen peroxide by the finely-divided metal and the absorptive capacity of the plates for hydrogen and oxygen when the plates were used as electrodes in a storage cell charged with dilute sulphuric acid. The alteration of the overvoltage shown by the plates in dilute acid was also examined, but no definite results were obtained, although both the anodic and the cathodic decomposition potentials with polished platinum differ considerably from those shown by platinised electrodes.

The results of the hydrogen peroxide decompositions and the storage capacities of the plates as electrodes are shown in the set of curves. The first two sets were obtained with platinum, the third with silver, and the last with palladium. In all cases the abscissae represent the temperatures to which the plates were

heated, and the ordinates correspond either with cubic centimetres of oxygen evolved per minute, or with the time in minutes taken for the storage cell, constructed of the given plates in dilute sulphuric acid, to fall to a potential of 0.4 volt when discharged through a fixed external resistance. The full-line curves represent the results of the peroxide decompositions, and the dotted curves the



results for cell capacity. The capacity measurements were satisfactory only in the case of platinum, as palladium absorbs an excessive quantity of hydrogen, whilst silver unites with the radicle of the acid used.

The first set of curves for platinum was obtained by using plates platinised in the ordinary way, that is, by reversing the current every half minute during the deposition of the platinum black. It was thought that such plates might contain considerable quantities of chlorine, so a second set of measurements was carried

out in which the current was not reversed during the plating and the cathode was kept in a separate vessel from the anode, the two being connected by means of a syphon. By this method, not only is no chlorine evolved at the cathode, but also the possible diffusion of chlorine from the anode is practically prevented. It will be seen from the curves that the catalytic action of the chlorine-free plate is not augmented to the same extent by low temperature as is the case with the plate which possibly contained occluded chlorine. Further evidence of the presence of chlorine in the plate was obtained by plating with reversal of current and then—after washing—by heating the plate in a closed vessel through which a current of air was drawn, the air being afterwards passed through a starch-iodide solution. Under these conditions the starch gave a blue colour, due to the liberation of iodine by the chlorine, but when the platinum was deposited free from chlorine in the manner indicated, no blue colour was obtained.

Considering the catalytic action of the metals as shown by the full-line curves, two points should be noted; first, the temporary increase in activity which occurs after heating to certain temperatures, and secondly, the gradual falling off in activity as high temperatures are reached. The first effect may be explained by the evolution of occluded gas, the escape of which would not only increase the roughness of the plates, but also, in some cases, help the catalysis by the removal of a catalytic poison. The falling off in catalytic power which takes place when high temperatures are reached is probably due to a decrease in the specific surface of the deposited metal, accompanied by an alteration in the size and number of points at which the liberated oxygen can escape in the form of bubbles. The storage capacity of the plates when used as electrodes in a storage cell also falls off, after heating, in the manner shown by the dotted curves in the first two figures. In this case also the same explanation will hold good, that is, the decrease in specific surface produced by heating will be accompanied by a falling off in the occlusive power of the plates for gases, and therefore also in their storage capacity when used as electrodes in a storage cell.

If the view of the decrease of specific surface be accepted, then it should be possible to detect such an alteration by application of the microscope. Photomicrographs of the plates, made before and after heating, were unsatisfactory owing to the lack of contrast between the different parts of the plated surface. The plan was therefore adopted of photographing a plated wire against a bright background, so that in effect a silhouette of the plated wire was obtained; the wire was then heated, usually by an electric current, and then rephotographed. Wires of platinum, silver, iron, and

copper were examined in this manner; with the exception of platinum, the wires were heated in an atmosphere of hydrogen to avoid oxidation. Substances of low melting point were not investigated owing to the difficulty of judging the temperature when heating by the current, that is, in all cases the melting point of the wire was considerably above red heat. The results obtained are shown in the table. The figures given are proportional to the diameters of the plated wires before and after heating, the diameter of the unplated wire being taken as unity in each case. In all cases a portion of the plating was removed from the freshly-coated wire, so that the original diameter was always shown in the photographs, thus providing a standard and avoiding errors of focus. The results clearly indicate that heating is in all cases followed by a decrease of specific surface.

	Diameter before heating.	Diameter after heating to dull redness.
Platinum .....	1.31	1.15
Silver .....	1.21	1.11
Iron .....	2.00	1.41
Copper .....	1.66	1.36

Faraday (*Phil. Trans.*, 1857, **147**, 145) observed that a gold leaf mounted on glass and heated to about 500° lost its green colour when viewed by transmitted light and became transparent, the green colour being restored on burnishing. Turner (*Proc. Roy. Soc.*, 1908, [A], **81**, 301) repeated the experiment and took photographs of the transparent gold. By this means he showed that the film had ceased to be continuous and had gathered itself up into a network of gold strands, the effect of burnishing being to flatten out the strands again so as to reproduce the original surface. Beilby (*Proc. Roy. Soc.*, 1904, **72**, 226), and Chapman and Porter (*ibid.*, 1910, [A], **83**, 65) investigated the same phenomenon and advanced the view that the effect was produced by the surface tension of the metal, which was able to operate owing to the lower rigidity produced by heating. Chapman and Porter also showed that a freely-suspended leaf merely contracts in area but remains continuous on heating, the network effect only being produced when the leaf was mounted on glass. With the thickness of leaf they employed, the contraction started at the definite temperature of 340°.

A different explanation of the observed effects also seems possible. A very finely-divided metal may have a considerably lower melting point than the same substance in bulk, and as a result of this incipient melting the smaller particles would attach themselves to the larger, which would not only grow, but would also become cemented together by the liquid smaller particles, the whole effect corresponding with a low-temperature sintering of the finely-

divided metal. The increased vapour pressure of a finely-divided liquid in the state of mist, where the large drops grow at the expense of the smaller, and the increased solubility obtained by using a substance in a fine state of division, are corresponding phenomena. Therefore it may be assumed that fine division alters the melting point as well as the vapour pressure and the solubility. Whatever the cause may be, there seems little doubt that finely-divided metals show a very considerable decrease of specific surface when heated to temperatures much below their usual melting points.

Further evidence in support of the theory can be deduced from the fact that finely-divided metals, when used as catalysts, are always more active when produced by reduction at low temperatures, the same being true in connexion with the activity of the metallic pyrophori made from nickel or iron. In both cases the metal produced at a low temperature has a high specific surface, which is considerably reduced by the particles melting together at higher temperatures. It should be noted that the sintering effect may be to some extent prevented if the catalytic metal is mounted on a carrier such as asbestos, for under such conditions the metallic particles are to a certain extent kept separate from each other. It is also interesting to note that, as a rule, surface catalysts are substances of very high melting point, and that the optimum temperature for any given catalyst is always considerably below its melting point.

#### EXPERIMENTAL.

The plates used measured 25 by 35 mm. and were fitted with wires of the same metal welded on to them. The electrolysing solutions were chlorides in the case of palladium and platinum, cyanide in that of silver, and sulphates in the cases of copper and iron. After deposition of the metal, the surface was cleaned by using the plates as electrodes in a solution of dilute sulphuric acid; the plates were then washed in distilled water and dried. The heating of the plates was carried out in a small resistance furnace, the temperature being noted by means of a thermo-couple.

The storage cell was filled with *N*-sulphuric acid, and the plates were charged by connecting them with a 2-volt accumulator for fifteen seconds; the current was then broken and the cell allowed to discharge itself through a voltmeter of 390 ohms resistance and graduated to 1/100th of a volt. The time required for the cell voltage to fall to 0.4 volt was taken as an indication of the storage capacity of the plates.

Before the plates were used for the decomposition of hydrogen peroxide, the platinum and palladium plates were saturated with

oxygen, and the silver with hydrogen, by using them as electrodes in a cell filled with dilute sulphuric acid. The peroxide used was of approximately two-volume strength, and the same solution was always employed for any series of measurements, the strength being checked from time to time by titration with potassium permanganate. Twenty-five c.c. of the solution were placed in a wide test-tube, and allowed to stand in a bath until it attained a temperature of  $18^{\circ}$ ; the electrode was then introduced and the tube was closed by a rubber stopper connected with a three-way tap open to the air. Fifteen seconds after the introduction of the electrode, the tap was turned so as to make connexion between the test-tube and a Hempel gas-burette. The quantity of oxygen evolved per minute was noted, the figure plotted being the mean value obtained during the first three minutes.

The wires used in obtaining the photomicrographs were plated in the same way as the plates; the diameter varied between 0.15 and 0.3 mm. The platinum wire was merely held between terminals fitted into the edge of a slip of wood mounted on the microscope stage. A slip of paper was placed beneath the wire and illuminated from below so as to form a bright background, against which the wire was silhouetted. The heating was carried out by means of the electric current, no attempt being made to measure the temperature, but, judging by the colour of the glow, it always lay between  $650^{\circ}$  and  $850^{\circ}$ . The copper, silver, and iron wires were all mounted—after plating—between two steel wires passed through a rubber stopper. During heating, the stopper carrying the wires was used to close an inverted bottle, through which a stream of purified dry hydrogen was passed, the heated wire being in all cases allowed to cool in the atmosphere of hydrogen. After heating, the rubber stopper was removed from the bottle, mounted on the stage, and the wire photographed.

#### *Conclusion.*

The metals, silver, copper, iron, platinum, and palladium, when deposited electrolytically in a fine state of division, show the phenomenon of sintering at temperatures considerably below their ordinary melting points. It is thought that this effect may be parallel to the abnormal vapour pressure and solubility of finely-divided material. The effect probably has considerable influence on the optimum temperature of a finely-divided metal when used as a catalyst.

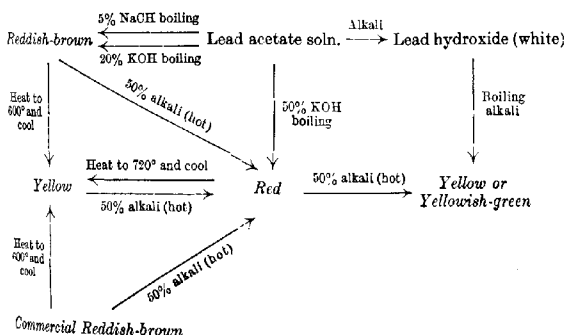
CXCII.—*Physical Chemistry of the Oxides of Lead.*  
*Part I. The Solubility of Lead Monoxide.*

By SAMUEL GLASSTONE.

THIS series of studies was originally undertaken with the object of investigating the affinity relationships between the various oxides of lead by electrochemical and other methods. It was found necessary to investigate the subject of lead monoxide in detail, owing to its existence in several coloured modifications. The first part of this work, consisting mainly of solubility determinations, is now described.

Red and yellow forms of lead monoxide were prepared by Geuther (*Annalen*, 1883, **219**, 56) by the action of alkalis on solutions of lead salts; in addition, it was found that a reddish-brown form, similar in colour to commercial litharge, could be prepared from these reagents. When a boiling 15 per cent. (or more dilute) solution of lead acetate is added to a boiling 5 per cent. (or more dilute) solution of sodium hydroxide, this reddish-brown form is directly precipitated. With potassium hydroxide (compare Vinkelblech, *Annalen*, 1837, **21**, 21), provided both solutions are boiling, the formation of the reddish-brown oxide is independent of the concentration; the colour, however, becomes more and more red until, when a 50–60 per cent. solution of potassium hydroxide is used, it is identical with that of Geuther's red oxide. The reddish-brown form is thus probably the finely divided red modification.

The relationships between the various forms of lead monoxide may be set out as follows:



The facts that any form of lead monoxide, when heated with



concentrated alkali hydroxide (50 per cent. or more), gives the red form, and that all forms on grinding give a brownish-yellow powder, suggested the possibility of a closer relationship between the forms of lead monoxide than that of allotropy, as worked out by Ruer (*Zeitsch. anorg. Chem.*, 1906, **50**, 265).

#### *Preparation of Forms of Lead Monoxide.*

The products were in each case washed with boiling water by decantation to remove the finer particles, then transferred to a Buchner funnel, well washed, and finally dried in a vacuum over calcium chloride.

No. 1. *Reddish-brown*.—A solution of 20 grams of sodium hydroxide in 400 c.c. of water was heated to the boiling point and treated gradually with a boiling solution of 60 grams of lead acetate in 400 c.c. of water.

No. 2. *Yellowish-green*.—To a solution of 30 grams of sodium hydroxide in 200 c.c. of water at 90° was slowly added a solution of 35 grams of lead acetate in 150 c.c. of water. The mixture was boiled until all the hydroxide had changed to a heavy, greenish-yellow solid, which settled to the bottom of the reaction vessel (a porcelain basin).

No. 3. *Red*.—120 Grams of sodium hydroxide dissolved in 180 c.c. of hot water were treated with a hot solution of 100 grams of lead acetate in 150 c.c. of water. The mixture was boiled for about an hour and stirred very frequently, small amounts of water being added to make up for the loss by evaporation. The yellow solid was completely converted into the red form.

No. 4. *Reddish-brown (prepared by means of potassium hydroxide)*.—The quantities recorded in No. 2 were employed, but potassium hydroxide replaced sodium hydroxide, and both solutions were boiling while being mixed.

No. 5. *Yellowish-green (prepared by means of potassium hydroxide)*.—The quantities used were exactly as in No. 4; the solutions, however, were mixed at a temperature below the boiling point and then boiled as in No. 2.

No. 6. *Lemon-yellow*.—Obtained by heating any of the other forms to 700° and allowing to cool (Ruer, *loc. cit.*).

No. 7. *Pure commercial lead monoxide*.—Reddish-brown flakes.

No. 8. *Brownish-yellow powder made by grinding the red form* No. 3 (compare Geuther, *loc. cit.*).

These specimens were all analysed, the lead being estimated gravimetrically as the sulphate. The percentage of lead found

varied from 92.62 to 92.83 (PbO requires Pb = 92.83 per cent.); traces of moisture accounted for the low results.

#### *Microscopic Examination.*

The red form (No. 3) consisted of the largest particles, mainly  $3\mu$  to  $5\mu$ , which, on being heated to  $700^\circ$  and then cooled (No. 6), gave larger, yellow agglomerates ( $10\mu$  to  $20\mu$ ); the latter easily broke down under gentle pressure into particles smaller than those of the original red form ( $0.7\mu$  to  $1.5\mu$ ). Products No. 2 and No. 5 were similar to No. 6. The reddish-brown oxides (Nos. 1, 4, 7) consisted of particles smaller than those of the red form ( $1\mu$  to  $2\mu$ ), but of the same order as the finer particles of the yellow forms. It is believed that the particles into which the yellow agglomerates easily disrupt are also reddish-brown in colour, for the yellow form, when gently pressed on paper or in the mortar, gives a brown powder. The brown powder obtained by grinding any form of lead monoxide consisted almost uniformly of particles  $0.7\mu$  in diameter. All the specimens may possibly have contained particles smaller than  $0.7\mu$  which were not visible under the microscope. That such small particles are present is shown by the fact that freshly-prepared suspensions of lead monoxide in dilute alkali hydroxide solution often cannot be clarified by filtration through paper.

In accordance with the work of Ostwald (*Zeitsch. physikal. Chem.*, 1900, **34**, 495) and others, we should expect to find differences in solubility between the various forms of lead monoxide depending on the size of the particles. The red form should have the lowest solubility, and the reddish-brown forms higher values. The case of the yellow and yellowish-green forms is more uncertain. If the effect of shaking with a solvent is to break up the agglomerates (compare Hulett and Allen, *J. Amer. Chem. Soc.*, 1902, **24**, 667), these forms should have a solubility almost the same as that of the reddish-brown form; gentle stirring of the solvent over the surface of the solid would probably give lower values.

#### *Solubility Determinations.*

The solvent chosen was a *N*-solution of sodium hydroxide (free from carbonate), which was made by decomposing with water sodium amalgam that had been prepared by the electrolytic method (compare Ming Chow, *J. Amer. Chem. Soc.*, 1920, **42**, 488).

About 5 grams of lead oxide were shaken, (a) gently, in glass vessels tied to the spokes of a wheel which revolved at 24 revs.

per minute, and (b) vigorously, in bottles placed in a motor-driven shaking-machine, with 20 or 30 c.c. of *N*-sodium hydroxide free from carbonate. After fourteen days, a portion of the clear liquid was drawn off without filtration (as filter-paper adsorbs lead in alkaline solution to a considerable extent), and the lead estimated gravimetrically as the sulphate. The solubilities of the various forms (numbered as above) are given in Table I.

TABLE I.

Temperature 20°.

Gram-mol. of PbO dissolved per litre of *N*-NaOH.

	Gentle shaking.	Vigorous shaking.
No. 1. ....	0.049	0.054
2. ....	0.048	0.054
3. ....	0.029	0.033
4. ....	0.049	
5. ....	0.049	
6. ....	0.047	
7. ....	0.049	
8. ....	0.040	

*Solubility of the Reddish-brown and Yellow Forms.*—The identical solubility of the yellow and reddish-brown forms may be explained on the assumption that the yellow agglomerates break down into small particles which are identical with those present in the reddish-brown forms. If these solutions of the reddish-brown and yellow forms were kept in contact with the respective oxides, a slow decrease in solubility was noted from 0.054 to 0.047 gram-mol. per litre, and in some cases to 0.042 gram-mol. per litre. The rate of decrease depended on the previous history of the specimen (that is, on the amount of very finely divided matter present) and on the ratio of solid phase to liquid phase present. In some cases a considerable time elapsed before the decrease became manifest, but in every case where the yellow or reddish-brown oxides were left in contact (without shaking) with *N*-sodium hydroxide containing 0.050 gram-mol. of lead oxide per litre, this decrease was eventually noticed. The equilibrium solubility of these forms is evidently lower than the values obtained with shaking; during the shake, small particles are being continually rubbed off, and high solubility values are therefore obtained, but when the solution is at rest these particles gradually disappear, being redeposited on the larger ones, and the solubility value falls.

In order to determine the equilibrium solubility of the reddish-brown and yellow forms, shaking must be avoided, so an arrangement was made by which the liquid could be gently stirred over the surface of the solid without disturbing the latter. Air free

from carbon dioxide and saturated with water vapour to the extent of the vapour pressure of *N*-sodium hydroxide, was gently bubbled through a bottle containing (a) yellow lead monoxide and *N*-sodium hydroxide, and (b) reddish-brown lead monoxide and *N*-sodium hydroxide. The experiment was carried out at room temperature, which did not vary very much from 20°. Portions of the clear liquor were withdrawn after every three or four days and analysed until constant values were obtained.

In both cases the solubility reached 0.039 gram-mol. of lead oxide per litre, and this may be taken as the solubility of the majority of the particles present in the reddish-brown and yellow forms of lead monoxide.

*Solubility of the Red Form.*—In this case the solubility showed a tendency to increase with keeping, possibly due to the slow solubility of the red form. More definite values should thus be obtained by placing *N*-sodium hydroxide supersaturated with respect to the red lead oxide in contact with the solid red form: the lead oxide content of the solution should then decrease until the equilibrium value is reached.

*N*-Sodium hydroxide was saturated with lead oxide to the extent of 0.048 gram-mol. per litre by shaking with the reddish-brown form, and a quantity of the red lead monoxide was placed in this solution. The mixture was gently stirred by the air-current method, and solubility determinations were made from time to time. The final value obtained in this way was 0.035 gram-mol. of lead oxide per litre, which is taken as the solubility of the red lead oxide in *N*-sodium hydroxide. This difference in solubility found between the various forms, namely, 0.039 and 0.035, is one that is readily accounted for on the grounds of varying size of particles. We have already seen that the red form of lead monoxide, if ground, gives a brown powder with a solubility of 0.040 gram-mol. per litre in *N*-sodium hydroxide (Table I).

Jones (*Zeitsch. physikal. Chem.*, 1913, **82**, 448) has developed a formula connecting the solubility of a finely-divided powder with the size of the particles, which resembles that of Ostwald (*ibid.*, 1900, **34**, 495), except that the integer 2 replaces 3. The later formula is simplified for the purpose of the subject now under discussion in the form :

$$\frac{RT}{M} \log_e \frac{s_r}{s_\infty} = \frac{2\sigma}{r\rho}$$

where *R*, *T* have their usual meaning, *M* is the molecular weight of the dissolved substance, *σ* the energy per unit surface of separation of solid and solution, *ρ* the density of the solid, *s<sub>r</sub>* and *s<sub>∞</sub>* the concentrations of the solute when spherical particles of radius *r*,

and plane surfaces of the solid are in contact with the solution;  $s_{\infty}$  is the solubility in a normally saturated solution (Hulett and Allen, *loc. cit.*). In the present case, if we assume that in the red form the particles are large enough to be considered to have plane surfaces, we can put  $s_{\infty}$  as equal to 0.035 gram-mol. per litre. Specimens of reddish-brown and yellow lead monoxide contain particles  $0.7\mu$  in diameter, and we will assume that it is these particles which give the measured solubility of 0.039 gram-mol. per litre. By substituting these values for  $s_r$  and  $s_{\infty}$ , and putting  $r = 0.35 \times 10^{-4}$  cm.,  $R = 8.31 \times 10^7$  ergs,  $M$  (for lead oxide) = 223,  $\rho = 9$  (approx.), and  $T = 293^\circ$  Abs., we obtain for  $\sigma$ , the energy located at the surface of discontinuity between lead monoxide and *N*-sodium hydroxide, the value 1860 ergs per sq. cm. at  $20^\circ$ . This value is of the same order as those calculated for other substances by Jones (*loc. cit.*). The value of  $\sigma$  between lead monoxide and water is probably not very different from the value calculated for *N*-sodium hydroxide, as the ratio of the solubilities is almost the same in both solvents for particles of equal size (see below).

It may be emphasised here that the explanation of solubility differences that has been developed, is put forward not only for the reddish-brown forms of lead monoxide, but also for the yellow and greenish-yellow forms which have been presumed to be polymorphic modifications by previous authors.

#### *Dissociation Constant of Lead Monoxide as an Acid.*

Berl and Austerweil (*Zeitsch. Elektrochem.*, 1907, **13**, 165) calculated the dissociation constant of lead monoxide as a monobasic acid, from the values of its solubility in sodium hydroxide solutions of varying concentrations. This result is incorrect for two reasons, (a) the solubility values used were those obtained after vigorous shaking for some hours, and (b) the solubility of lead monoxide in water as used by these authors is much too high (compare Pleissner, *Arb. Kaiser. Gesundh.-Amt.*, 1907, **26**, 384). A series of determinations of the solubility of lead monoxide in solutions of sodium hydroxide was therefore carried out by the method described on page 1693. Solutions of sodium hydroxide (free from carbon dioxide) of varying concentrations were shaken with dry lead hydroxide in order to obtain solutions supersaturated with respect to the monoxide (the small amount of water added in this way was regarded as negligible). The clear liquids were drawn off into bottles containing the red lead monoxide, which were then placed in a thermostat at  $25^\circ$ . The solutions were analysed from time to time, until constant values were obtained.

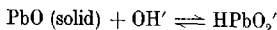
In the more concentrated solutions the lead was estimated as sulphate. With sodium hydroxide solutions of normality 0.2 or less, the lead was precipitated as peroxide by means of bromine water, the precipitate was well washed with boiling water (cold water tends to give colloidal filtrates), and the lead estimated iodometrically.

TABLE II.

All concentrations are expressed in gram-mol. per litre at 25°.

Concn. of PbO in NaOH. solution. (C)	Sodium plumbite. (c <sub>1</sub> - c <sub>0</sub> ).	Residual NaOH. (C - c <sub>1</sub> + c <sub>0</sub> ).	$k = \frac{\text{Concn. of HPbO}_2'}{\text{Concn. of OH}'} = \frac{(c_1 - c_0)}{(C - c_1 + c_0)}$
0.9985	0.0349	0.03464	0.9639
0.4993	0.0195	0.01924	0.4801
0.1177	0.00506	0.00481	0.1129
0.0499	0.00230	0.00204	0.0479
			0.0359
			0.0401
			0.0425
			0.0426

The solution of lead oxide in sodium hydroxide may be represented by the equation



(Bert and Austerweil, *loc. cit.*; Hantzsch, *Zeitsch. anorg. Chem.*, 1902, **30**, 305), the equilibrium constant being given by

$$k = [\text{HPbO}_2'] / [\text{OH}']$$

The concentration of plumbite ion (HPbO<sub>2</sub>') may be assumed equal to the additional solubility of lead monoxide in sodium hydroxide solution, over and above that of the ordinary solubility in water, multiplied by the degree of ionisation of sodium plumbite at each concentration. If c<sub>1</sub> is the solubility of lead monoxide in sodium hydroxide of concentration C, α<sub>1</sub> and α the degrees of dissociation of plumbite and hydroxide solutions respectively, and c<sub>0</sub> the solubility of lead oxide in water, we have

$$[\text{HPbO}_2'] = (c_1 - c_0)\alpha_1.$$

The total concentration of OH' originally present is given by Cα, but as a certain quantity is used up in forming plumbite, the actual concentration is given by (C - c<sub>1</sub> + c<sub>0</sub>)α. Since sodium hydroxide and plumbite contain a common ion, they will probably be ionised to the same extent in a solution containing both of them. For purposes of calculation we will assume that α and α<sub>1</sub> are equal, an assumption which may not be quite true in the more concentrated

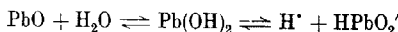
solutions. We thus obtain the expression,  $k = \frac{(c_1 - c_0)}{(C - c_1 + c_0)}$ .

In connexion with the solubility in water of lead monoxide, there is some uncertainty. Fleissner has shown that determinations of solubility by the conductivity method are useless, and only

those in which lead has been estimated by chemical methods are worth consideration. Berl and Austerweil (*loc. cit.*) found a solubility of  $1.02 \times 10^{-3}$  gram-mol. per litre for lead oxide made by heating lead carbonate at  $400^\circ$ . This figure is very much higher than any other to be found in the literature for the solubility of lead oxide in water, and is possibly due to exceptional fineness of division. Milbauer (*Chem. Zeit.*, 1909, **33**, 960) has found that the lead oxide prepared from lead carbonate absorbs oxygen in the formation of red lead, far more rapidly than any other form of the monoxide: this fact confirms the above suggestion. The value for the solubility of lead oxide used in these calculations was obtained as follows. In some work to be published later, the author has found that the ratio of the solubilities of lead hydroxide and the red monoxide in sodium hydroxide of the same concentration is about 1.75 and is almost independent of the concentration of the sodium hydroxide. Assuming this ratio to hold in the case of water, and using Pleissner's (*loc. cit.*) most trustworthy value for the solubility of lead hydroxide,  $0.45 \times 10^{-3}$  gram-mol. per litre (at  $18^\circ$ ), we arrive at a value of  $0.25 \times 10^{-3}$  gram-mol. per litre for the solubility of the red lead monoxide. This value agrees very well with Berl and Austerweil's value for the solubility of lead oxide in water at  $18^\circ$ ,  $0.26 \times 10^{-3}$  gram-mol. per litre. Although these authors did not use this value, it is probably the most accurate available and will be used in these calculations for  $25^\circ$ ; the difference of temperature will not cause serious errors. Attention may be directed to the fact that Pleissner obtained for the solubility of the yellow form a value of  $0.30 \times 10^{-3}$  gram-mol. per litre; the ratio between this and  $0.26 \times 10^{-3}$  is not very greatly different from that of 39 to 35, the ratio of the solubilities of the red and yellow forms of lead oxide in *N*-sodium hydroxide.

Using the values as explained, we arrive at the fifth column of Table II for the value of the equilibrium constant  $k$ . The first value 0.0359 is probably low for the reason that  $\alpha$  and  $\alpha_1$  are not equal in the more concentrated solution. The value for the constant  $k$  to be used in these calculations is 0.0425.

Lead monoxide in solution may be considered as follows:



(Hantzsch, *loc. cit.*), and the dissociation constant as an acid is given by

$$K_A = \frac{[\text{H}^+][\text{HPbO}_2']}{[\text{Pb}(\text{OH})_2]} = \frac{K_w[\text{HPbO}_2']}{[\text{Pb}(\text{OH})_2][\text{OH}']} = \frac{K_w k}{[\text{Pb}(\text{OH})_2]}$$

where  $K_w$ , the dissociation constant of water, is  $0.81 \times 10^{-14}$  at  $25^\circ$ . The value of  $[\text{Pb}(\text{OH})_2]$  is taken as equal to the solubility of lead

monoxide in water; substituting this and the known values of  $K_w$  and  $k$ , we obtain  $K_A = 1.32 \times 10^{-12}$ .

*Summary.*

- (1) The suggestion is put forward that the yellow forms of lead monoxide are really agglomerates of small particles, which are almost identical with the finely divided red form. Solubility determinations and microscopic examination confirm this view.
- (2) The energy at the surface of separation of lead monoxide and *N*-sodium hydroxide is calculated as 1860 ergs per sq. cm. at 20°. If water replaces sodium hydroxide solution, the value does not differ greatly.
- (3) The dissociation constant of the acid  $H \cdot HPbO_2$ , produced by dissolving lead oxide in water, is  $1.32 \times 10^{-12}$  at 25°.

The author wishes to thank Professor Allmand for suggesting this series of investigations, and for criticism and advice given throughout the course of this work.

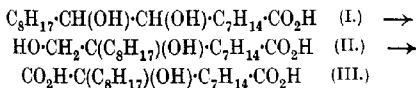
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[Received, May 9th, 1921.]

(CXIII.—*The Mechanism of the Action of Fused Alkalies. Part II. The Action of Fused Potassium Hydroxide on Phenylglyceric Acid.*

By (the late) HENRY RONDEL LE SUEUR and CYRIL  
CHRISTIAN WOOD.

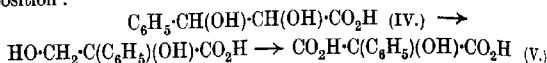
THE conversion of dihydroxystearic acid (I) into  $\alpha$ -hydroxy- $\alpha$ -stylobacic acid (III) by the action of molten potassium hydroxide (Le Sueur and Withers, T., 1914, 105, 2800) involves the preliminary formation of a dihydroxyoctyldecoic acid (II) isomeric with the first-named substance, followed by oxidation:



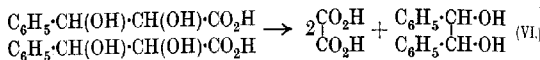
By similar transformations, dihydroxybehenic acid was converted into  $\alpha$ -hydroxy- $\alpha$ -octyldodecanedicarboxylic acid (*loc. cit.*), and it was therefore resolved to ascertain whether phenylglyceric acid



(IV), in which the octyl group is replaced by phenyl, and the remaining unsubstituted aliphatic chain is eliminated, would undergo conversion into phenyltartronic acid (V), or products of its decomposition :

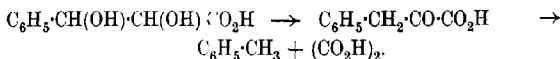


It soon became evident that the change takes an entirely different course, neither phenyltartronic acid, nor degradation products therefrom such as phenylglycollic acid and benzyl alcohol, being obtained. At a temperature approaching  $250^\circ$  approximately equivalent amounts of benzoic and oxalic acids were produced, whilst under less drastic treatment ( $160$ – $170^\circ$ ) the principal aromatic product was toluene, accompanied by an equivalent amount of oxalic acid and very much smaller quantities of benzoic, formic, and acetic acids; in each case 30–40 per cent. of the original material was lost. On heating the system at the lower temperature under reduced pressure, however, a remarkable alteration in the course of the change was effected, the aromatic group appearing as isohydrobenzoin (VI), accompanied by nearly two molecular proportions of oxalic acid and a subsidiary quantity of benzoic acid :



Under the conditions observed, almost all the water was removed from the system before the temperature had reached  $150^\circ$ , and as the visible action does not begin below that stage, it seems highly probable that the great divergence from previous experiments must be due to this cause. Examination was made for tartaric acid, which might have been expected to accompany isohydrobenzoin, but that substance could not be found.

The formation of toluene would be explained by simultaneous reduction and oxidation, recalling that by which benzyl alcohol and benzoic acid arise together from benzaldehyde, leading in this case to phenylpyruvic acid (VII) as an intermediate stage :



Search was accordingly made for phenylpyruvic acid, but it was only when phenylglyceric acid was heated under reflux during many hours with a concentrated solution of potassium hydroxide that a small quantity of material giving the characteristic coloration with ferric chloride was obtained.

The profound alterations consequent on varying the conditions of the foregoing oxidation emphasise once more the uncertainty of

molten potassium hydroxide in its action on organic substances, the result of which can be accepted only as corroborative evidence in questions of constitution when harmonising with those from sources less under suspicion.

#### EXPERIMENTAL.

A preliminary experiment showed that the action of fused potassium hydroxide on phenylglyceric acid does not give rise to effervescence until a temperature approaching  $150^{\circ}$  is reached, when the odour of toluene is noticeable; thereafter, at about  $180^{\circ}$ , the action becomes difficult to control, and the pasty mass remaining after nine minutes have elapsed in reaching  $200^{\circ}$  contains potassium benzoate and oxalate. More precise conditions were therefore defined.

*At a Temperature of  $160-170^{\circ}$ .*—Ten grams of phenylglyceric acid with 50 grams of potassium hydroxide and 20 c.c. of water in a retort connected with a condenser were heated during fifty-four minutes by a bath of fusible metal at  $160-170^{\circ}$ , action at first being very vigorous. Toluene (3.3 grams) passed over in the steam and, when isolated, distilled completely at  $110-111^{\circ}$  (Found: C = 91.3; H = 8.8.  $C_7H_8$  requires C = 91.3; H = 8.7 per cent.). The residue in the retort having been dissolved in water, aliquot parts of the solution were examined separately and quantitatively for benzoic, and for oxalic and formic acids, the amounts estimated being 0.68, 3.4, and 0.11 gram respectively; the presence of acetic acid was demonstrated qualitatively. Hence the toluene and oxalic acid were produced in equivalent amounts, and the extent of conversion was about 68 per cent.

*At a Temperature of  $240-250^{\circ}$ .*—Potassium hydroxide (50 grams) and water (20 c.c.) in a nickel crucible were heated by fusible metal, and when the temperature had reached  $240-250^{\circ}$  phenylglyceric acid (10 grams) was added in small quantities with continued stirring during twenty minutes, liberation of benzoic acid vapour being recognisable. The cold, faintly green product was dissolved in 150 c.c. of water and acidified with 68 c.c. of hydrochloric acid, when benzoic acid was precipitated; the quantity, making allowance for solubility in water, amounted to 4 grams, and the filtrate contained 3.1 grams of oxalic acid. Thus the acids were produced in approximately equivalent amounts, the deficit of benzoic acid being doubtless due to volatilisation during fusion; the extent of conversion was about 60 per cent.

*At  $170-180^{\circ}$ , under Reduced Pressure.*—Phenylglyceric acid (5 grams), potassium hydroxide (25 grams), and water (10 c.c.) were

heated in a distilling flask which was evacuated through a condenser. By controlling the temperature of the castor-oil bath at  $170-180^{\circ}$ , the pressure was maintained during ten minutes at 25 mm., but this reduction was not reached until almost all the water had been removed. The oil which distilled was negligible, and the colourless residue in the flask having been extracted with water and acidified, *isohydrobenzoin* (1.9 grams), benzoic acid (0.2 gram), and oxalic acid (1.2 grams) were recognised. Thus the quantity of *isohydrobenzoin* indicated a conversion of 65 per cent., but the amount of oxalic acid, whilst exceeding one equivalent, fell somewhat short of that corresponding with two molecular proportions.

Since benzoic acid and *isohydrobenzoin* melt at the same temperature ( $121^{\circ}$ ), identity of the latter substance was established by analysis and by determination of molecular weight in boiling acetone (Found: C = 78.60; H = 6.59. M = 213.  $C_{14}H_{14}O_2$  requires C = 78.50; H = 6.54 per cent. M = 214). The diacetyl derivative melted at  $117-118^{\circ}$  (Found: C = 72.29; H = 6.07.  $C_{18}H_{18}O_2$  requires C = 72.48; H = 6.04 per cent.).

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## Organic Chemistry.

**Chemistry of the Heptane Solution. II. Revision of the Physical Constants of Heptane.** E. KREMERS and R. KREMERS (*J. Amer. Pharm. Assoc.*, 1920, **9**, 860—864).—Fifteen specimens of the oleoresin of *Pinus sabiniana* were steam-distilled; the average yield was 7.8%. The distillates had  $d_{20}$  0.685, except one which was 0.686. The crude heptane was purified by successive shaking with concentrated sulphuric acid, fuming sulphuric acid, sodium carbonate, and potassium permanganate. The constants of the purified heptane were  $n_{20}$  1.3895; b. p. 97.33°/760 mm.;  $d_{20}$  0.68288;  $\gamma_{20}$  19.8 crgs;  $[\alpha]_D$  0. CHEMICAL ABSTRACTS.

**The Labile Nature of the Halogen Atoms in Substituted Nitromethanes.** ALEXANDER KILLEN MACBETH and DAVID DOUG PRATT (*T.*, 1921, **119**, 1356—1361).

**Ethyl Hydrogen Sulphate.** HORACE BARRATT DUNNICLIFF and GERALD SNOWDEN BUTLER (*T.*, 1921, **119**, 1384—1392).

**Ultrafiltration of Lecithin Sols.** H. BECHHOLD and S. M. NEUSCHLOSS (*Kolloid Zeitsch.*, 1921, **29**, 81—89).—The filtration of lecithin sols by ultra-filters under varying conditions has been investigated with the object of ascertaining the nature of lecithin emulsions. It is shown that a lecithin sol contains particles of very different sizes, and of these only the largest give rise to a turbidity which is recognisable by nephelometric methods. The quantity of the sol in a 1% solution recognisable by the nephelometer is 4% of the total amount. A portion of the lecithin is adsorbed by the filter when aqueous solutions are subjected to ultra-filtration; the quantity adsorbed becomes greater the greater the density of the filter. The slightly disperse lecithin particles are more strongly adsorbed than the highly disperse particles. In the ultrafiltration of lecithin emulsions the quantity of material which passes through the filter depends on the pressure under which filtration takes place, hence in the same filter by merely varying the pressure from 90 grams/cm.<sup>2</sup> to 2000 grams/cm.<sup>2</sup> it is possible to vary the filtrate from practically pure water to a solution which contains practically the whole of the lecithin. From this it is deduced that the surface tension at the interface water-lecithin is exceedingly small. The value has been calculated as less than 16 C.G.S. units.

J. F. S.

**The Quantitative Separation of the Lead Salts of the Saturated from the Less Unsaturated Fatty Acids.** ARMIN SEIDENBERG (*J. Amer. Chem. Soc.*, 1921, **43**, 1323—1336).—The lead salts of the acids are dissolved in a mixture of the three solvents, alcohol, chloroform, and ethyl ether, and the two latter more

VOL. CXX. i.

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volatile and powerful solvents are evaporated off until all the more insoluble salts are precipitated. This process was found to give sharper and more easily controlled separations than the methods commonly used. By its use practically a complete removal of all the salts of the saturated acids can be obtained from their solutions and from the solvent used in washing the precipitate. Within wide limits, the results are independent of the amounts of the fatty acids used.

From oils or fats containing the more unsaturated acids it was not possible to obtain the saturated fatty acids in an approximately pure state by either the fractionation method or the lead salt-ether method. On the other hand, when only the less unsaturated acids, such as oleic acid, are present, the saturated fatty acids as isolated were found to have practically no iodine number and to be readily soluble in light petroleum.

W. G.

**Configuration of  $\alpha\alpha'$ -Dibromo-dibasic Acids. I. The Di-bromoadipic Acids. Synthesis and Resolution of *trans*-cyclopentane-1:2:3-tricarboxylic Acid.** WILLIAM HENRY PERKIN, jun., and ERIC ROBINSON (T., 1921, 119, 1392—1399).

**The Mechanism of the Oxidation of Drying Oils as Elucidated by a Study of the True Oxygen Absorption. II. Linolenic and Linolic Acids.** SAMUEL COFFEY (T., 1921, 119, 1408—1415).

**Preparation of a Petrol from a Vegetable Oil.** ALPHONSE MAILHE (*Compt. rend.*, 1921, 173, 358—359).—When linseed oil is passed over a mixture of electrolytic copper and magnesium oxide as a catalyst at 550—650° and the product hydrogenated over reduced nickel, a mixture of aromatic and cyclic hydrocarbons is obtained. Benzene, toluene, xylene, cyclohexane, and methylcyclohexane were identified.

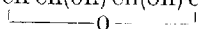
W. G.

**Production of Acetaldehyde from Acetylene.** SOCIÉTÉ ANONYME DE PRODUITS CHIMIQUES (ÉTABLISSEMENTS MALÉTRA) (Brit. Pat. 140784).—In the preparation of acetaldehyde from acetylene, with an acid mercuric sulphate solution as catalyst, the process is rendered practically continuous by the periodic addition of ferric oxide to the bath. For example, 9.26 kilos. of mercury are triturated with 7.4 kilos. of ferric oxide and 70 kilos. of concentrated sulphuric acid; 191 kilos. of water are added, and the mixture is heated to 70—83°, preferably about 80°. Acetylene is admitted to the catalytic liquid thus prepared, and water is added from time to time equivalent to the amount of acetaldehyde produced, so that the concentration of the sulphuric acid is maintained at 30—35% of the total catalytic liquid. After 280 kilos. of acetaldehyde have been obtained, a further 7.4 kilos. of ferric oxide and 13.34 kilos. of sulphuric acid are added and the operation may be repeated to an almost unlimited extent. In practice, after about ten operations, it is desirable to decant the liquid from the

small quantity of tarry matter formed. It is essential that the acetylene be purified before use, particularly from hydrogen phosphide.

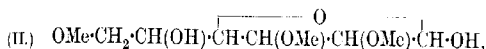
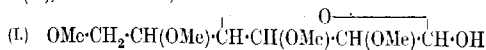
G. F. M.

**Structure of Cellobiose.** M. BERGMANN (*Naturwiss.*, 1921, 9, 308—309; from *Chem. Zentr.*, 1921, iii, 214; cf. this vol., i, 307).—Cellobial, which is structurally identical with glucal, has in the reducing half of the molecule a double linking between carbon atoms 1 and 2 and an "oxygen bridge" between 1 and 4; the hydroxyl group in position 3 is not substituted. Since the carbon atom 6 does not take part in the formation of a disaccharide, and since in the formation of cellobial from cellobiose displacement of the glucosidic attachment does not occur, the formula for cellobiose must be  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{O}\cdot\text{C}_6\text{H}_{11}\text{O}_5)\cdot\text{CH}\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}\cdot\text{OH}$ .

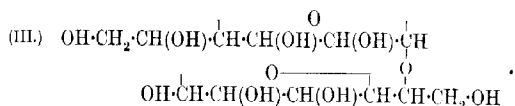


G. W. R.

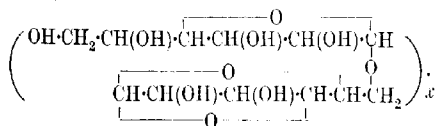
**Constitution of Starch and Glycogen.** P. KARRER (*Naturwiss.*, 1921, 9, 399—403; from *Chem. Zentr.*, 1921, iii, 214; cf. this vol., i, 310—313).—A summary of earlier work. By acid hydrolysis of heptamethyl methylcelloside, tetramethylglucose (I), and trimethylglucose (II), are obtained,



whereby the formula for cellobiose must be (III),



The analogies in the behaviour of starch and  $\alpha$ -amylose extend to their reactions with alkaline-earth hydroxides.  $\alpha$ -Octamylose gives a precipitate with barium hydroxide solution. A similar compound is obtained with  $\alpha$ -tetra-amylose and may be precipitated by addition of a little ethyl alcohol.  $\alpha$ -Tetramylose by distillation in a vacuum gives a good yield of *levoglucosan*. The formula for starch should be



The position of the anhydride bridge is undetermined.

G. W. R.

**Plant Colloids. XI. Electro-disintegration of Starch Solutions.** M. SAMEC and ANKA MAYER (*Koll. Chem. Beihefte*, 1921, 13, 272—288; cf. this vol., i, 400).—By electro-disintegration

d d 2

of starch solutions, a retrograded solution of amyloses was obtained. This solution yields a blue coloration with iodine (amylo-amylose), has  $\alpha_D + 189^\circ$ , and a mean molecular weight of about 80,000. This fraction constitutes 17% of the starch substance; it is electro-neutral and corresponds with Maquenne's amylose. The amylopectin which has thus been separated from the amylo-amyloses yields a reddish-violet colour with iodine. In 2% solution, it has an electrical conductivity  $8.3 \times 10^{-5}$  and a hydrogen-ion concentration  $2.4 \times 10^{-4}N$ . It has a mean molecular weight of 113,000. By heating amylopectin with water in neutral solution under pressure, non-retrograded erythroamyloses are formed. These give a wine-red coloration with iodine, have  $\alpha_D + 195-196^\circ$ , and a mean molecular weight of about 130,000-140,000. In solution with its own acid reaction, amylopectin is not only hydrolysed but also disaggregated and yields within six hours 80% of dialysable products. The colloidal residue from this has a mean molecular weight of 57,000, but the iodine coloration and the optical rotation are the same as those of the erythroamyloses above. The presence of erythroamyloses in solution is substantiated colorimetrically. From the change in the iodine coloration with increasing addition of iodine the quantity relationship of the iodine-amyloamylose complex is deduced as  $(C_6H_{10}O_5)_2I$ . The erythroamyloses appear to take up a larger quantity of iodine. The name "soluble starch" for the erythroamyloses is justified. The "elementary molecule" of starch may possibly have a molecular weight below 2000. J. F. S.

**Constitution of "Iodide of Starch."** A. LOTTERMOSER (*Zeitsch. angew. Chem.*, 1921, **34**, 427-428).—From the results of electric potential and other physical measurements, the author concludes that the supposition of Biltz and others that the so-called "iodide of starch" is an adsorption compound of starch and molecular iodine is justified. Neither iodion nor potassium iodide is adsorbed by starch to any appreciable extent, but experiments indicated that in  $N/100$  or less potassium iodide solutions there is a noticeable adsorption of tri-iodion. In  $N/10$ - or  $N/5$ -solutions, this is, however, so small as to be negligible. In general, the results confirmed the statement of Mylius that for the formation of the blue colour the presence of iodion is necessary, since it participates, if only very temporarily, in the adsorption. G. F. M.

**Wood Cellulose.** EMIL HEUSER and E. BOEDEKER (*Zeitsch. angew. Chem.*, 1921, **34**, 461-464).—Contrary to the views of Cross and Bevan and others, the authors suggest the hypothesis that all plant cellulose, from whatever source derived, is a chemical individual, and that there is only one variety of cellulose, namely, that expressed by the formula  $(C_6H_{10}O_5)_n$ . It has already been shown (Heuser and Haug, *Zeitsch. angew. Chem.*, 1918, **31**, 99) that purified straw cellulose is identical with cotton cellulose and the identity of wood cellulose, suitably purified from pentosans, etc., with the latter is now demonstrated. A bleached wood cellulose was freed from resin and fat by extraction with a mixture of benzene and alcohol,

and was then extracted three times with boiling 6% sodium hydroxide (or alternatively with cold 17% sodium hydroxide) whereby the pentosan content was reduced from 4.06% to 1.8—1.92%. At the same time both the ash and the copper number were reduced, the latter from 4.07 to 0.8—0.9. The pentosan remains therefore the only appreciable impurity, and by sufficiently repeated alkali extraction this can be eliminated to such an extent that on distillation with 12% hydrochloric acid by Tollens and Kröber's method no furfuraldehyde is obtained, although of course there is considerable loss in cellulose by this treatment. The hydrolysis of the wood cellulose purified as above by triple alkali extraction was compared with that of cotton cellulose, dextrose being estimated periodically both by copper reduction and polarimetrically. The hydrolysis was carried out in cold concentrated hydrochloric acid by Willstätter and Zechmeister's method. In each case the maximum glucose reading was reached in 16.5 hours, and about 97.5% was obtained, showing that the course of the hydrolysis was with both cellulose preparations identical. Further, from the wood cellulose hydrolysis 94.2% of pure dextrose was actually isolated and identified by its osazone.

G. F. M.

**Nature of the Swelling Process. II.** F. KNOEVENAGEL and ROBERT MOTZ (*Koll. Chem. Beihefte*, 1921, **13**, 233—241; cf. this vol., i, 402).—Partition experiments between swollen cellulose acetate hydrogel and aqueous solutions of aniline, phenol, methyl tartrate, and ethyl tartrate of small concentrations have been carried out at 18° and 30—33°, both acetone-soluble and chloroform-soluble cellulose acetate being used in the experiments. It is shown that a partition occurs after twenty-four hours in keeping with Henry's law. The establishment of such an equilibrium points to the occurrence of a process of solution in both phases; that is, no adsorption takes place in the swollen cellulose acetate. Special experiments in the case of ethyl tartrate show that unswollen cellulose acetate does not remove any of the ester from its aqueous solution in short periods of time, exactly in the same way as it was previously shown (*loc. cit.*) that unswollen cellulose acetate in aqueous solutions of dyes remains completely uncoloured. That is, only after months or years does unswollen cellulose acetate come into equilibrium with the dye solution, whilst swollen cellulose acetate, under similar conditions, and according to the extent of the swelling, attains an equilibrium with the dye solution in a few minutes or hours and is dyed in full colours.

J. F. S.

**Nature of the Swelling Process. III.** E. KNOEVENAGEL and ALBERT BREGENZER (*Koll. Chem. Beihefte*, 1921, **13**, 242—261; cf. preceding abstract).—The swelling of various kinds of cellulose acetate in binary mixtures of alcohol with benzene, nitrobenzene, and carbon tetrachloride respectively has been measured at ordinary temperatures, as well as the surface tension of all four solvents, and the binary mixtures named above. The degree of swelling of cellulose acetate in the four simple solvents decreases in the order: nitrobenzene, benzene, alcohol, carbon tetrachloride,



so that of these only nitrobenzene can be regarded as a strong swelling medium for cellulose acetate; carbon tetrachloride acts very slightly in this respect. The surface tension of the four solvents falls in the order: nitrobenzene, benzene, carbon tetrachloride, alcohol. In the binary mixtures, the alcohol lowers the capillarity of the other constituent. The amount of lowering of the capillarity is greatest for the first addition of the second constituent and is greater the greater the difference between the surface tension of alcohol and that of the second constituent. A qualitative relationship between the lowering of the surface tension and the degree of swelling in the binary mixtures has been established. The stronger the capillary action of the alcohol, the more does the degree of swelling increase. The action of the alcohol, however, is in opposition to the swelling action of the other component; consequently there exists for each binary mixture a composition which gives an optimum swelling effect. J. F. S.

**Nature of the Swelling Process. IV. Swelling and Internal Friction in the System Cellulose Acetate-Nitrobenzene-Alcohol.** E. KNOFVENAGEL and ALBERT BREGENZER (*Koll. Chem. Beihefte*, 1921, **13**, 262—271; cf. preceding abstracts).—The viscosity of solutions of various concentrations of cellulose acetate in mixtures of nitrobenzene and ethyl alcohol containing 90, 70, and 50 vol. % respectively of the former substance has been measured at 25°; the specific gravity of all the solutions has also been determined. It is shown that the viscosity curve for the weaker swelling liquid always lies below that of the stronger swelling liquid. The ratio of the viscosities of any two equally concentrated cellulose acetate solutions in different mixtures of nitrobenzene and alcohol is constant for all concentrations of cellulose acetate. The viscosity of a given binary mixture increases with increasing cellulose acetate concentration, and is approximately proportional to the logarithm of the internal friction. J. F. S.

**Cellulose. IV. Depolymerisation of Ethylcellulose.** KURT HESS, WALTER WITTELSBACH, and ERNST MESSMER (*Zeitsch. angew. Chem.*, 1921, **34**, 449—454; see this vol., i, 401).—Trustworthy conclusions as to the constitution of cellulose from the products of the acetolysis of alkylated celluloses can only be drawn when alkylation has been conducted in such a way as to exclude the probability of the disruption of glucoside or ether-like linkings. Under these conditions, the limit of alkylation is reached when two ethyl groups per  $C_6H_{10}O_5$  have been taken up. The resulting diethylcellulose is an individual substance and when subjected to acetolysis depolymerisation occurs with the absorption of one acetyl group for each  $C_6H_8O_3(OEt)_2$ , and without the generation of a free aldehyde group. The acetylated product is easily hydrolysed by methyl alcoholic ammonia and gives a product of the same empirical composition as the original material and with a molecular weight in dilute solution of 800—900, rapidly increasing with increasing concentration owing to association. This substance therefore contains at most four hexose residues, and since free

aldehyde groups are absent it must be assumed that these structural units are held together in the original cellulose molecule by some other means than a "glucoside" linking. Although approximately identical molecular weights were found for different preparations of the substance, differences in optical rotation and melting point exclude the possibility of their absolute identity, and indicate that the depolymerisation is accompanied by isomerisation. Further acetolysis results in the formation of ethylated acetyl-hexoses which on hydrolysis give a syrup which appeared to be mainly a mixture of triethyl- and diethyl-glucose, the latter preponderating, although only the former has yet been isolated in crystalline form. The presence or otherwise of other ethylated glucoses in the syrup and its actual percentage composition are still to be determined, but the results so far do not show complete agreement with those of either Denham and Woodhouse (T., 1921, 119, 77) or Irvine (T., 1920, 117, 1489).  
G. F. M.

**Are Hydrocelluloses Simple Substances?** H. OST and R. BREITSCHNEIDER (*Zeitsch. angew. Chem.*, 1921, 34, 422—423).—From evidence obtained by a comparative examination of hydrocellulose, made by Girard's method, and cellulose, purified as for nitration purposes, before and after digestion with boiling lime-water containing 0.5—1.0% of calcium oxide, the authors draw the conclusion that hydrocelluloses are simple substances and are not mixtures of cellulose and cellulose dextrins as suggested by Hauser and Herzfeld, and by Schwalbe and Becker (cf. A., 1915, i, 441; 1920, i, 474).

The hydrocellulose and cellulose contained 0.24—0.34% and 0.30% of ash, and 3.17—3.94% and 5.39% of moisture respectively, and during their digestion in boiling lime-water for twelve hours 24.4% of hydrocellulose and 15.8% of cellulose dissolved. At the same time, the "copper numbers" of the hydrocellulose and cellulose changed from 6.69 to 0.91 and 2.05 to 0.61, and the "cellulose numbers" from 0.14 to 0.29 and 0.30 to 0.36 respectively.

Although the "copper" and "cellulose" numbers of the final residues from hydrocellulose and cellulose are similar, the hydrocellulose residue is essentially different from cellulose and is similar to the original hydrocellulose. This is shown by the viscosity of its solution in cuprammonium hydroxide solution and the solubility of its acetate (acetylation is carried out by means of acetic acid, acetic anhydride, and zinc chloride as catalyst) in acetone. [See, further, *J. Soc. Chem. Ind.*, 1921, 634A.]  
A. J. H.

**Pseudo-bases. III. Dialkylaminomethyl Alkyl Ethers and Sulphides.** CHARLES MAXWELL MCLEOD and GERTRUDE MAUD ROBINSON (T., 1921, 119, 1470—1476).

**Derivatives of some Amino-acids.** L. HUGOUNENQ and G. FLORENCE (*Bull. Soc. Chim. Biol.*, 1921, 3, 283—285).—A description of the action of chromium hydroxide on aqueous solutions

of some amino-acids, and of the preparation of double salts by the action of calcium hydroxide on the hydrochlorides of aspartic acid and glycine.

C. R. H.

**The Constitution of the Nitroprussides. II. Alkylation of Nitroprussic Acid.** GEORGE JOSEPH BURROWS and EUSTACE EBENEZER TURNER (T., 1921, 119, 1450—1452).

**Manufacture of Hydrocarbons [Naphthenes].** CHARLES WEIZMANN and DAVID ALLISTON LEGG (Brit. Pat. 165452).—A mixture of naphthenes is obtained by polymerising by means of aluminium chloride the mixture of butylenes obtained by the dehydration of *n*-butyl alcohol. In carrying out the process the vapour of *n*-butyl alcohol is passed at atmospheric pressure through a tube containing pumice coated with aluminium oxide heated at 250—320°, when a mixture of  $\beta$ - and  $\alpha$ -butylene is formed containing about 80% of the former. At higher temperatures, for example, 360—390°, the product is practically all  $\beta$ -butylene, and the yield nearly theoretical. The liquefied butylene is then treated with anhydrous aluminium chloride in the proportion of 28 grams of the former to 0.5 gram of the latter and the temperature is kept below -10°. If an autoclave is used a temperature as high as 15° is admissible. Polymerisation is complete in about two hours and a practically quantitative yield of naphthenes is obtained, distilling as follows: 8 grams at 260—290°/17 mm., 13 grams at 270—350°/17 mm., and 5 grams above 350°/17 mm.

G. F. M.

**Nitration of Toluene.** M. GIUA (*Gazzetta*, 1921, 51, ii, 113—115).—The author expresses agreement with Drew's statement (T., 1920, 117, 1615; cf. also Brady and Taylor, T., 1920, 117, 876) that the compound, m. p. 79.5°, isolated from the oily residues obtained in the purification of 2:4:6-trinitrotoluene is not the 2:3:6-compound, as supposed by Molinari and Giua (A., 1915, i, 790), but an additive compound of 2:3:4- and 3:4:6-trinitrotoluenes.

Doubt is cast on Drew's statement (*loc. cit.*) that 2:3:6-trinitrotoluene is formed when toluene is nitrated directly. Drew isolated this compound by treating the mixed products with hydrazine hydrate; which reacts with the 2:3:4- and 3:4:6-compounds, but leaves the 2:3:6-compound unaltered. The author finds, however, that the 2:3:6-compound should be easily attacked by hydrazine hydrate under the conditions employed by Drew, so that the latter's so-called 2:3:6-compound is probably the 2:3:4-compound, these two having the same melting point.

[The author gives Drew's name throughout this paper as Barry.]

T. H. P.

**Reduction of Trinitrotoluene.** ELIAS BIELOUSS (Brit. Pat. 166934; addition to 137529).—The process of reducing trinitrotoluene to triaminotoluene by means of iron and hydrochloric acid, as described in the earlier patent, is improved by using only a small quantity of hydrochloric acid as in the technical

reduction of nitrobenzene. The iron compounds are thus obtained as a sludge which can be removed by filtration from the triaminotoluene solution. In the example given, the quantities suggested are 230 kilos. of trinitrotoluene, 700 kilos. of iron turnings, 800 litres of water, and 20 litres of 35% hydrochloric acid, the reaction mixture being maintained at 60–80°. Triaminotoluene serves as a dye for cotton, silk, and wool, as a photographic developer, and as an intermediate.

G. F. M.

**9:10-Dihydrophenanthrene.** HERBERT HENSTOCK (T., 1921, 119, 1461–1463).

**Influence of Substituents on Reactions. VI. Nitration of Substituted Acetanilides.** HARTWIG FRANZEN and ERWIN ENGEL (*J. pr. Chem.*, 1921, 102, 156–186).—The nitration of acetanilide and its *o*-methyl-, *o*-chloro-, *o*-bromo-, *o*-ethoxy-, and *m*-chloro-derivatives has been investigated. In general, the finely-divided acetanilide (33.75 grams) is gradually added to a well-stirred mixture of fuming nitric acid (*d* 1.505, 65 c.c.) and glacial acetic acid (35 c.c.) which is cooled in a freezing mixture, the rate of addition being so regulated that the temperature does not exceed 1°. The product is allowed to remain in the cooling mixture during twelve hours so that it gradually attains the atmospheric temperature; it is then poured into water (350 c.c.) and the precipitate is collected and dried. Under these conditions, nitration is complete except in the cases of *o*-bromo- and *m*-chloro-acetanilide, for which reaction must be continued during twenty-four hours. In certain cases, the method of Witt and Utermann (A., 1907, i, 27), which involves the use of nitric acid, glacial acetic acid, and acetic anhydride, has also been employed. In this manner, the nitrated anilide is not quantitatively precipitated, but the losses are shown to be distributed in general uniformly over the various isomerides. The quantitative separation of the *o*- and *p*-isomerides is effected by the Witt-Utermann method (*loc. cit.*), the necessary corrections being worked out experimentally for the individual cases.

The authors are led to the following conclusions. The introduction of methyl, chlorine, or bromine in position 2 and of chlorine in position 3 of acetanilide increases the ease of replacement of the hydrogen atom in position 6 by nitric acid and diminishes that of the hydrogen atom in position 4; in this respect, bromine has a less marked action than chlorine or methyl, which have approximately the same effect. The introduction of the ethoxy-group in the 2-position of acetanilide so greatly diminishes the reactivity of the hydrogen atom in position 6 towards nitric acid that the *o*-nitro-derivative is not produced; the replaceability of hydrogen atom 4 is likewise diminished, whilst that of atom 3 is very markedly increased. The addition of ammonium nitrate to the nitrating mixture of nitric acid and glacial acetic acid causes an alteration in the relative amounts of the isomerides produced. In the nitration of acetanilides with nitric and acetic acids and acetic anhydride compared with the action in the absence of the latter, a displace-

*d d*\*

ment of the relative quantities of the isomerides is observed of such a kind that the directive action of the acetyl-amino-group is more pronounced.

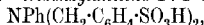
The following compounds have not been described previously: 2-chloro-6-nitroacetanilide, yellow needles, m. p. 130–132°; 2-chloro-6-nitroaniline, yellow needles, m. p. 76°; 2-bromo-6-nitroacetanilide, yellow needles, m. p. 190°. H. W.

**The Method of Witt and Utermann for the Separation of *o*- and *p*-Nitroacetanilides.** HARTWIG FRANZEN and FRITZ HELWERT (*J. pr. Chem.*, 1921, **102**, 187–193).—Witt and Utermann (A., 1907, i, 27) have described a process for the separation of *o*- and *p*-nitroacetanilides which depends on the solubility of the former and the insolubility of the latter in a mixture of potassium hydroxide solution (50%, 1 vol.), water (4 vols.), and alcohol (1 vol.) at 0°. The applicability of the method to other nitroacetanilides has now been investigated. All the *o*-nitroacetanilides dissolve in the mixture with greater or less readiness; on the other hand, certain para-derivatives are very appreciably soluble. In general, it is shown that *m*-nitroacetanilides can be separated in this manner from the ortho-derivatives, but this case is likely to be encountered seldom in practice. In the majority of instances, *p*-nitroacetanilides can be separated from the corresponding ortho-compounds; exceptions are, however, to be expected with the halogenated *o*-nitroacetanilides. In the naphthalene series, the separation of 2- and 4-nitroacetanaphthalides is improbable, but 1-nitro- $\beta$ -acetanaphthalide should be separable from the other nitro- $\beta$ -acetanaphthalides. A further limitation to the applicability of the method is probably imposed by the sparing solubility of certain *o*-nitroacetyl-amino-compounds in the solution.

The volume of the mixture necessary for the solution of one gram of the various anilides at 0° is shown by the figures in parenthesis: *o*-nitroacetanilide (20), 6-nitro-*o*-acetotoluidide (40), 2-nitro-*p*-acetotoluidide (83), 1-nitro- $\beta$ -acetanaphthalide (52), 2-nitro- $\alpha$ -acetanaphthalide (150), 4-nitro- $\alpha$ -acetanaphthalide (312). In certain cases, at any rate, it is possible to replace potassium hydroxide by sodium hydroxide, but not by ammonia. H. W.

**Amines. IX. Alkylation of Aromatic Amines by Heating with Aliphatic Alcohols.** ARTHUR J. HILL and JOHN J. DONLEAVY (*J. Ind. Eng. Chem.*, 1921, **13**, 504–509; see A., 1920, i, 671).—The formation of tertiary bases by heating isomeric toluidines with ethyl alcohol or *n*-butyl alcohol was investigated and found to be promoted by certain catalysts (cupric chloride, sodium bromide, and calcium chloride) and by the use of a large excess of the alcohol. The mixtures were heated at 175° to 180° for eight hours. The yields varied from 50% in the case of di-*n*-butyl-*o*-toluidine to 90% for diethyl-*p*-toluidine; *o*-toluidine was the least reactive of the isomerides. Two new amines were prepared by the method, di-*n*-butyl-*o*-toluidine, b. p. 256–258°/755 mm., and di-*n*-butyl-*m*-toluidine, b. p. 278–280°/755 mm. W. P. S.

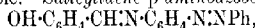
**Preparation of Dibenzylaniline-4 : 4'-disulphonic Acid and Ethylbenzylaniline-4'-sulphonic Acid.** SOCIETY OF CHEMICAL INDUSTRY IN BASLE (Swiss Pats. 87882 and 87883; from *Chem. Zentr.*, 1921, iv, 259).—*Dibenzylaniline-4 : 4'-disulphonic acid*,



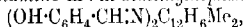
is prepared by the condensation of two molecules of sodium  $\omega$ -chlorobenzyl-*p*-sulphonate with one molecule of aniline in aqueous solution. *Benzylethylaniline-4'-sulphonic acid*,  $\text{NEtPh}\cdot\text{CH}_2\text{-C}_6\text{H}_4\text{-SO}_3\text{H}$ , is similarly prepared by condensation of sodium  $\omega$ -chlorobenzyl-*p*-sulphonate with monoethylaniline. G. W. R.

**Phototropy.** PATRICK GALLAGHER (*Bull. Soc. chim.*, 1921, [iv] 29, 683—696).—From a study of a number of salicylideneamines the author was not able to trace any direct relationship between phototropy and chemical constitution. The changes in colour are not to be attributed to purely chemical changes in the molecule. The salicylideneamines were prepared by condensation in alcoholic solution and the following are described.

*Salicylidenenitro- $\psi$ -cumidine*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Me}_2\cdot\text{NO}_2$ , m. p.  $120^\circ$ , is not phototropic. *Salicylidene- $\alpha$ -chloro- $\beta$ -naphthylamine*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{C}_{10}\text{H}_7\text{Cl}$ , m. p.  $156^\circ$ , is slightly phototropic. *Salicylidene- $\alpha$ -aminocinnamic acid*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ , m. p.  $231^\circ$ , is phototropic. *Salicylidene-*p*-phenetidine*, m. p.  $94^\circ$ , is not phototropic. *Salicylidene-*p*-aminobenzaldehyde*, m. p.  $99^\circ$ , is not phototropic. *Salicylidene-*p*-aminoazobenzene*,



m. p.  $156^\circ$ , is not phototropic. *Disalicylidene-2 : 4-diaminoazobenzene*,  $\text{NPh}\cdot\text{N}\cdot\text{C}_6\text{H}_3(\text{N}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OH})_2$ , m. p.  $150^\circ$ , is not phototropic. Ethyl salicylidene-*p*-aminobenzoate is phototropic, but the methyl ester is not. *Salicylidene-1 : 2 : 4-nitrotoluidine*, m. p.  $129^\circ$ , is thermotropic, but not phototropic. *Salicylidene-1 : 3 : 6-nitrotoluidine*, m. p.  $125^\circ$ , is not phototropic. *Salicylidene-1 : 4 : 2-nitrotoluidine*, m. p.  $112^\circ$ , is very thermotropic, but not phototropic. *Disalicylidene-*p* : *p*-diamino-*m* : *m*-dimethyldiphenyl*,

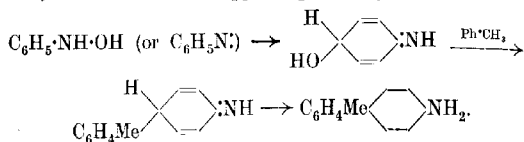


m. p.  $203^\circ$ , is thermotropic, but not phototropic. *Salicylidene-1 : 2-naphthalenediamine*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{C}_{10}\text{H}_6\text{NH}_2$ , m. p.  $162^\circ$ , is not phototropic. *Disalicylidenenaphthalene-1 : 2-diamine*, m. p.  $213^\circ$ , the -1 : 4-diamine, m. p.  $142^\circ$ , the -1 : 5-diamine, m. p.  $220^\circ$ , the 1 : 8-diamine, m. p.  $199^\circ$ , and the -2 : 7-diamine, m. p.  $203^\circ$ , are not phototropic. *Salicylidene- $\alpha$ -phenylenediamine*, m. p.  $90^\circ$ , is very phototropic at low temperatures, but it having been shown by Kenier and Sheppard (*T.*, 1909, 95, 441, 1943) that the disalicylidene derivative is not phototropic, the monosalicylidene derivative was condensed with a number of aldehydes; in no case, however, was phototropy observed. *Benzylidenesalicylidene- $\alpha$ -phenylenediamine*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{CHPh}$ , has m. p.  $214^\circ$ ; *m-tolylidenesalicylidene- $\alpha$ -phenylenediamine* has m. p.  $238^\circ$ ; *p-tolylidenesalicylidene- $\alpha$ -phenylenediamine* has m. p.  $135^\circ$ ; *salicylideneanisylidene- $\alpha$ -phenylenediamine* has m. p.  $130^\circ$ ; *salicylideneperonylidene- $\alpha$ -phenylenediamine* has m. p.  $130^\circ$ .

*phenylenediamine* has m. p. 140°; and *salicylidene-m-methoxy-salicylidene-o-phenylenediamine* has m. p. 125°.

Benzylamine condenses with nitrosobenzene in alcoholic solution to give a red oil, which is apparently *s*-phenylbenzylidiazine; when this substance is reduced with zinc and alcoholic sodium hydroxide it yields *s*-phenylbenzylhydrazine, m. p. 35–36°. W. G.

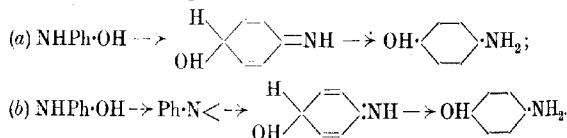
**Transformation of certain Aromatic Compounds.** F. BAMBERGER (*J. pr. Chem.*, 1921, **102**, 267–275).—In order to explain the production of 4-*p*-aminophenyltoluene (Bamberger, A., 1895, i, 289; Kühling, *ibid.*, i, 182) by the action of aluminium chloride on a mixture of phenylhydroxylamine and toluene, Kliegl and Huber (A., 1920, i, 835) have assumed the intermediate production of the residue,  $-C_6H_4 \cdot NH-$ . According to the author, the reaction can be readily explained by the annexed scheme, which has been applied previously to similar cases:



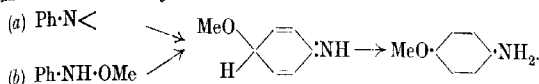
This conception has the advantage that it can be applied to a large number of other cases, such as the transformation of azoxybenzene to *p*-hydroxyazobenzene or benzeneazodiphenyl, of nitrobenzene to *o*-nitrosophenol, of phenylnitroamine to *o*-nitroaniline, of  $\alpha$ -naphthylnitroamine to  $\beta$ -naphthaquinone- $\alpha$ -diazide, of dimethylaniline oxide to *o*-dimethylaminophenol, of nitrosomethylaniline to *p*-nitrosomonomethylaniline, and of phenylsulphamic acid to *o*-anilinesulphonic acid. H. W.

#### Arylhydroxylamines and Arylazides. A Comparison.

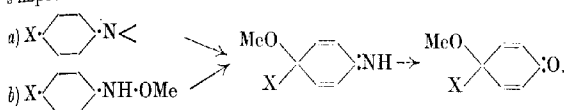
EUGEN BAMBERGER (*Annalen*, 1921, **424**, 233–296).—A general review of the chemistry of the arylhydroxylamines, especially from the point of view of the mechanism whereby, under the influence of various reagents, transformations occur which involve substitution in the nucleus. Eight typical reactions are discussed, and it is shown that in every case at least two alternative mechanisms are possible. These are (a) that isomeric change occurs to an imino- $\psi$ -quinol, which, provided the necessary hydrogen atom is present, passes into the benzenoid form, (b) that water is eliminated with the formation of an arylimide,  $Ar \cdot N <$ , which then takes up the elements of water (or of the reagent), forming the same quinonoid derivative. For example:



The author considers the second mechanism to be the more probable, one reason being that it avoids the necessity for supposing that when, for instance, a mixture of methyl alcohol and sulphuric acid acts on a hydroxylamine, a methoxy-group wanders from a methoxylamine residue initially formed :

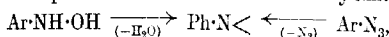


The same holds in the case of para-substituted arylhydroxylamines, in which rearrangement from the quinonoid to the benzenoid forms is impossible :



The products in this case are the ethers of  $\psi$ -quinols or of imino- $\psi$ -quinols.

With the view of obtaining more light on these questions, the behaviour towards various reagents of certain arylhydroxylamines and arylazides have now been examined comparatively, particular attention being directed to the relative quantities of the various products formed. This was essential, because, whilst the undoubted qualitative similarity between the two sets of reactions might be traceable to the production in each case of the arylimide,



an alternative hypothesis had been suggested by Friedländer and Zeitlin (A., 1894, i, 184), namely, that the azide first passed into the hydroxylamine. This (according to Friedländer and Zeitlin) is why Griess obtained *p*-aminophenol from phenylazide by the action of dilute sulphuric acid (A., 1886, i, 459).

The following is a summary of the comparative experiments :

(1) (Cf. A., 1912, i, 691.) Phenylhydroxylamine (20 grams) and dilute sulphuric acid (1 : 10), heated for forty-five minutes on a water-bath, gave *p*-aminophenol (14 grams), *p*-aminophenol-*o*-sulphonic acid (0.5 gram), and azoxybenzene (2 grams). (1a) \* Phenylazide (10 grams) and dilute sulphuric acid (1 : 3 by volume), boiled for twenty-four hours, gave *p*-aminophenol (1 gram) and *p*-aminophenol-*o*-sulphonic acid, but no azoxybenzene. (2) (*ibid.*) Phenylhydroxylamine (6 grams), phenol, and dilute sulphuric acid (1 : 3 by volume), boiled for five minutes, gave *p*-amino-*p'*-hydroxydiphenyl (0.8–0.9 gram), aniline, azoxybenzene (?), and amphoteric matter, *n*<sub>D</sub> about 179°. (2a) \* Phenylazide (6 grams), phenol, and dilute sulphuric acid (1 : 3 by volume), boiled for one and three-quarter hours, gave *p*-amino-*p'*-hydroxydiphenyl (0.4 gram), *p*-hydroxydiphenylamine (trace), aniline (doubtful trace), and amphoteric

\* Denotes reactions which have not previously been qualitatively investigated.

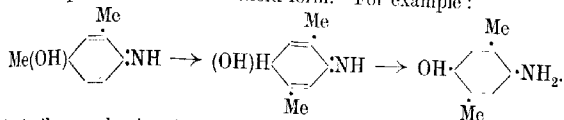


matter, m. p. about  $182^{\circ}$ , but no azoxybenzene. (3) (Cf. A., 1894, i, 520.) Phenylhydroxylamine (100 grams), alcohol (2400 c.c.), and sulphuric acid (50 c.c.) after twenty-six hours on the water-bath, gave *p*-phenetidine (45 grams), *o*-phenetidine (8 grams), *p*- and *o*-aminophenol (3.5 grams), aniline (4 grams), azoxybenzene (14 grams), and *p*-aminodiphenylamine (very little). (3a) \* Phenylazide (15 grams), ethyl alcohol (105 c.c.), and sulphuric acid (52 c.c.), after twenty-five hours on the water-bath, gave *p*-phenetidine (5.5 grams), *o*-phenetidine (0.3 gram), *p*-aminophenol (0.5 gram), aniline (0.4 gram), *p*-aminodiphenylamine (very little), and phenol (by odour only), but no azoxybenzene. (3') \* Phenylhydroxylamine (100 grams), methyl alcohol (2400 c.c.), and sulphuric acid (50 c.c.), after eight hours on the water-bath, gave *p*-anisidine (21 grams), *o*-anisidine (6 grams), *p*-aminophenol (0.2 gram), *p*-aminophenol-*o*-sulphonic acid, aniline (small quantity), azoxybenzene (17 grams), and much gum. (3'a) \* Phenylazide (5 grams), methyl alcohol (50 c.c.), and sulphuric acid (25 grams), after twenty-two hours on a water-bath, gave *p*-anisidine (1.9 grams), (probably) *o*-anisidine and aniline (0.4 gram together), *p*-aminophenol, but no azoxybenzene. (4) (Cf. following abstract.) Phenylhydroxylamine (60 grams) and concentrated hydrochloric acid (saturated at  $0^{\circ}$ ), after thirty days at  $0^{\circ}$ , gave *p*-chloroaniline (37 grams), *o*-chloroaniline (15 grams), *op*-dichloroaniline (0.2 gram), azoxybenzene (0.2 gram), and doubtful traces of aniline, *o*-aminophenol, and *s*-trichloroaniline. (4a) (Cf. A., 1886, i, 459.) Phenylazide (131 grams) and concentrated hydrochloric acid, first at  $0^{\circ}$  and finally on the water-bath, gave *p*-chloroaniline (86 grams), *o*-chloroaniline (25 grams), *op*-dichloroaniline (0.3 gram), and aniline (0.2 gram), but no azoxybenzene. (5) *o*-Tolylhydroxylamine \* (34 grams), methyl alcohol (1000 c.c.), and sulphuric acid (17 c.c.), after thirty days at room temperature, gave 5-methoxy-*o*-toluidine (13 grams), 6-amino-*m*-cresol (0.2 gram), and azoxytoluene (0.7 gram). (5a) \* *o*-Tolylazide (20 grams), ethyl alcohol (2 volumes), and sulphuric acid (1 volume), after twenty-four hours in the cold and subsequent heating on the water-bath, gave 5-ethoxy-*o*-toluidine (4.8 grams), 6-amino-*m*-cresol (1.2 grams), and a small quantity of phenolic material, but no azoxytoluene. (6) \* *o*-Tolylhydroxylamine (61 grams) and dilute sulphuric acid (1 : 10 by volume), after forty-five minutes on the water-bath, gave 6-amino-*m*-cresol (20.4 grams), *o*-toluidine (1.3 grams), and azoxytoluene (7 grams). (6a) *o*-Tolylazide and sulphuric acid gave 6-amino-*m*-cresol (cf. Friedländer and Zeitlin, *loc. cit.*). (7) (Cf. following abstract.) *o*-Tolylhydroxylamine (30 grams) and concentrated hydrochloric acid (saturated at  $0^{\circ}$ ) after thirty days at winter temperatures gave 5-chloro-*o*-toluidine (13 grams), 3-chloro-*o*-toluidine (0.3 gram), 4-chloro-*o*-toluidine (1 gram), and azoxytoluene (0.2—0.3 gram). (7a) \* *o*-Tolylazide (120 grams) and concentrated hydrochloric acid (saturated at  $0^{\circ}$ ), after eight days in the cold, gave 5-chloro-*o*-toluidine (100—110 grams), 3-chloro-*o*-toluidine, but no azoxytoluene. (8) \* *m*-Tolylhydroxylamine (30.7 grams), ethyl alcohol (900 c.c.), and sulphuric acid (15 c.c.), after keeping for fifteen days in the dark,

gave 6-ethoxy-*m*-toluidine (3.7 grams), 5-amino-*o*-cresol (very little), and azoxytoluene (3.4 grams). (8a)\* *m*-Tolylazide (10 grams), ethyl alcohol (2 volumes), and sulphuric acid (1 volume), after three days' keeping in the cold and fifteen hours' subsequent heating on the water-bath, gave 6-ethoxy-*m*-toluidine (1.4 grams), 5-amino-*o*-cresol (2.5 grams), but no azoxytoluene. (8')\* *m*-Tolylhydroxylamine (32 grams), methyl alcohol (300 c.c.), and sulphuric acid (5 c.c.), after three months in the dark, gave 6-methoxy-*m*-toluidine (more than 10 grams), 5-amino-*o*-cresol (small amount), and azoxytoluene. (8'a)\* *m*-Tolylazide (8 grams), methyl alcohol (2 volumes), and sulphuric acid (1 volume), after five hours at room temperature and three hours' subsequent heating, gave 6-methoxy-*m*-toluidine (more than 1.7 grams), 5-amino-*o*-cresol (2.6 grams), and a trace of a phenolic substance, but no azoxytoluene. (9)\* *p*-Xyllylhydroxylamine (3.8 grams) and dilute sulphuric acid (1:10 by volume), after boiling for thirty-five minutes, gave 2-amino-*p*-5-xylol (2 grams), *p*-xyloquinol (1.1 grams), and a small amount of azoxy-*p*-xylene. (9a)\* *p*-Xyllylazide (10 grams) and dilute sulphuric acid (1:3 by volume), after boiling for fifteen hours, gave 2-amino-*p*-5-xylol (4.1 grams), *p*-xyloquinol (2.1 grams), but no azoxybenzene. (10)\* *p*-Xyllylhydroxylamine (5 grams), ethyl alcohol (175 c.c. of 96%), and sulphuric acid (2.5 c.c.), after three days at ordinary temperatures, gave 2-ethoxy-*p*-5-xylidine (1 gram) and azoxy-*p*-xylene (1.5 grams). (10a)\* *p*-Xyllylazide (15 grams), ethyl alcohol (2 volumes), and sulphuric acid (1 volume), after five hours at room temperature and two hours' gentle heating, gave 2-amino-*p*-5-xylol (5.2 grams), 2-ethoxy-*p*-5-xylidine (4.6 grams), 2-ethoxy-*p*-5-xylol (0.5 gram), and *p*-xyloquinol, but no azoxybenzene. (10')\* *p*-Xyllylhydroxylamine (11.1 grams), methyl alcohol (222 c.c.), and sulphuric acid (5.5 c.c.), after three weeks at room temperature, gave 2-methoxy-*p*-5-xylidine (theoretical amount) and traces of azoxy-*p*-xylene and *p*-xylidine. (10'a)\* *p*-Xyllylazide (5 grams), methyl alcohol (2 volumes), and sulphuric acid (1 volume), after five hours at room temperature and four hours' heating, gave 2-methoxy-*p*-5-xylidine (2.5 grams), 2-amino-*p*-5-xylol, but no azoxyxylene. (11)\* *p*-Chlorophenylhydroxylamine (10 grams) and dilute sulphuric acid (1:5 by volume), after twenty-five minutes at 40–50°, gave *p*-chloroaniline (1.2 grams), *op*-dichloroaniline (0.45 gram), *pp'*-dichloroazoxybenzene (5 grams), and traces of aniline. (11a)\* *p*-Chlorophenylazide (10 grams) and dilute sulphuric acid (1:5 by volume), boiled for fifteen hours, gave *p*-chloroaniline (0.9 gram), *op*-dichloroaniline (0.45 gram), and traces of aniline, but no dichloroazoxybenzene. (12) (Cf. following abstract.) *p*-Chlorophenylhydroxylamine (5.5 grams) and dilute sulphuric acid (1:3), after heating for twenty minutes at 50°, gave *op*-dichloroaniline (2.4 grams), *p*-chloroaniline (0.7 gram), and *pp'*-dichloroazoxybenzene (1.5 grams). (12a)\* *p*-Chlorophenylazide (5 grams) and dilute hydrochloric acid (20 grams concentrated acid and 40 grams of water), on boiling for twenty-two hours, gave *op*-dichloroaniline (1.8 grams), *p*-chloroaniline (0.45

gram), but no azoxybenzene derivative. (13)\* *p*-Bromophenylhydroxylamine (10 grams) and dilute sulphuric acid (1:5), heated for fifteen minutes at 40—50°, gave *op*-dibromoaniline (0.3 gram), *p*-bromoaniline (2.4 grams), 5-bromo-*o*-aminophenol (small quantity), and *pp'*-dibromoazoxybenzene (5 grams). (13a)\* *p*-Bromophenylazide (3 grams) and dilute sulphuric acid (1:5), on heating for fifteen hours, gave *op*-dibromoaniline, *p*-bromoaniline, a trace of 5-bromo-*o*-aminophenol, but no azoxybenzene derivative. (14) (Cf. A., 1912, i, 691.) *p*-Tolylhydroxylamine (14.5 grams) and dilute sulphuric acid (1:10 by volume), heated for forty minutes on the water-bath, gave toluquinol (9 grams), *p*-toluidine (2 grams), azoxy-*p*-toluene (0.9 gram), a small amount of *p*-cresol, and traces of 5-amino-*o*-cresol formed, probably, through the migration of the methyl group from the imino- $\psi$ -quinol ether intermediate formed (a better instance of this change is discussed below). (14a)\* *p*-Tolylazide (5 grams) and dilute sulphuric acid (1:3 by volume), after two hours' boiling, gave toluquinol (1 gram), *p*-toluidine (0.4 gram), and an odour of cresol, but no azoxytoluene or 5-amino-*o*-cresol. (14') *p*-Tolylhydroxylamine (30 grams) and dilute sulphuric acid (1:20 by volume), after fourteen hours' keeping at 18°, gave 11—12 grams of  $\psi$ -toluquinol (cf. A., 1912, i, 691). (14'')\* *p*-Tolylazide (22 grams) and sulphuric acid (1:1.75 water, by volume), after eleven hours' heating at 50—70°, gave  $\psi$ -toluquinol (0.6 gram), *p*-toluidine (5.4 grams), toluquinol (1 gram), *p*-cresol (0.1 gram), and traces of 5-amino-*o*-cresol, but no azoxy-derivative. (15) *p*-Tolylhydroxylamine and sulphuric acid gave "benzyleneimide" and its hydrate (*ibid.*). (15a)\* *p*-Tolylazide and sulphuric acid gave "benzyleneimide" and its hydrate. (16) *p*-Tolylhydroxylamine, *p*-nitrotoluene, and sulphuric acid gave 2-nitro-4'-amino-5-methyldiphenylmethane (*ibid.*). (16a)\* *p*-Tolylazide and sulphuric acid, after twenty-four hours at ordinary temperatures, yielded the same substance. (17) *p*-Tolylhydroxylamine (4.95 grams), phenol, and dilute sulphuric acid (1:3 by volume), on heating for twenty minutes, gave *p*-hydroxyphenyl-*p*-tolylamine (3.4 grams) and doubtful traces of toluquinol and azoxytoluene (*loc. cit.*). (17a)\* *p*-Tolylazide (6 grams), phenol, and dilute sulphuric acid (1:3 by volume), on heating for two hours, gave *p*-hydroxyphenyl-*p*-tolylamine (about 4 grams), toluquinol (0.3 gram), and some *p*-toluidine. (18)\* *p*-Tolylhydroxylamine (120 grams), methyl alcohol (1200 c.c.), and concentrated (100%) sulphuric acid (30 c.c.), after keeping for twenty-four hours at 10—20°, gave  $\psi$ -toluquinol 1-methyl ether (6.2 grams), *p*-toluidine (3 grams), and azoxy-*p*-toluene (65 grams). (18a)\* *p*-Tolylazide (73.5 grams), methyl alcohol (230 c.c.), and concentrated sulphuric acid (100%) (100 c.c.), after ten hours at 13—22° and two days at 25—30°, gave  $\psi$ -toluquinol 1-methyl ether (2.5 grams), *p*-toluidine (0.85 gram), but no azoxytoluene. (18'')\* *p*-Tolylhydroxylamine (150 grams), ethyl alcohol (1250 c.c.), and 100% sulphuric acid (35 grams), after fifteen hours at room temperature, gave  $\psi$ -toluquinol-1-ethyl ether (10.9 grams), *p*-toluidine (11.9 grams), and azoxy-*p*-toluene (78 grams). (18'a)\* *p*-Tolylazide (120 grams), ethyl

alcohol (370 c.c.), and 100% sulphuric acid (170 c.c.), after ten hours at 10–20° and a further 40 hours at 25–30°, gave  $\psi$ -tolu-quinol 1-ethyl ether (4 grams), *p*-toluidine (2.2 grams), but no azoxytoluene. (19) *m*-4-Xylylhydroxylamine (10 grams) and dilute sulphuric acid (1:10 by volume), on heating for twenty minutes on the water-bath, gave (A., 1912, i, 691) *p*-xylo-*p*-5-xynol. (19a) \* *m*-4-Xylylazide (60 grams) and dilute sulphuric acid (1:3 by volume), after six hours' heating, gave *m*-xyloquinol (0.4 gram), 2-amino-*p*-5-xynol (1.1 grams), *m*-4-xylidine, and an odour of xylenol, but no azoxyxylene. The production of the *p*-xylene derivative (2-amino-*p*-5-xynol) must be due to the migration of a radicle from the intermediate quinonoid products, for such an isomeric change is clearly necessary to enable them to pass into their benzenoid form. For example:

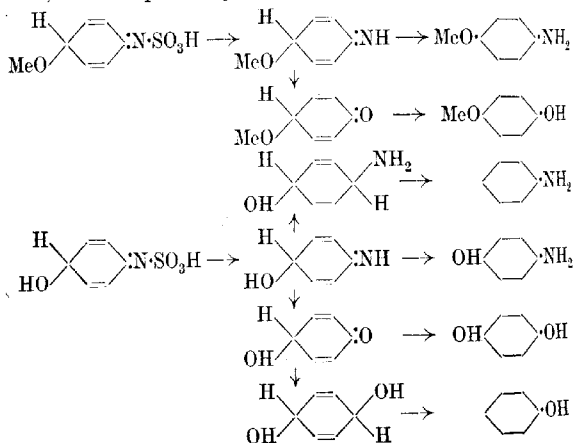


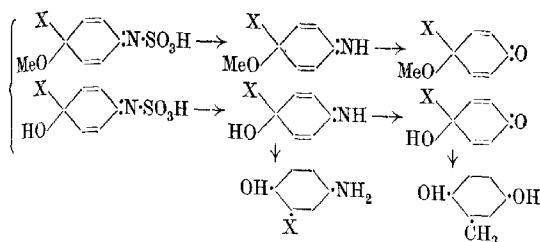
A similar mechanism is probably to be ascribed to the other cases of this kind mentioned in this paragraph. (19') *m*-4-Xylylhydroxylamine (35 grams) and dilute sulphuric acid (17.5 grams H<sub>2</sub>SO<sub>4</sub>+350 c.c. of water), after eight to ten days' keeping at 23–25°, gave (cf. A., 1907, i, 516–520)  $\psi$ -*m*-xyloquinol monohydrate (22 grams), *m*-4-xylidine (6 grams), azoxyxylene (2.5 grams), and traces of 2-amino-*p*-5-xynol. (19'a) \* *m*-4-Xylylazide (10 grams) and dilute sulphuric acid (1:2 by volume), after eleven hours at 65°, gave  $\psi$ -*m*-xyloquinol (1.2 grams), *m*-4-xylidine (0.7 gram), and *p*-xyloquinol (0.3 gram) besides an odour of xylenol and some amorphous acids and bases. (20) (Cf. *loc cit.*) *m*-4-Xylylhydroxylamine (100 grams), ethyl alcohol (900 c.c.), and sulphuric acid (30 c.c.), after three hours' heating on the water-bath, gave  $\psi$ -*m*-xyloquinol ethyl ether (30 grams), 4:6-diethoxy-*m*-xylene (7 grams), 6-ethoxy-*m*-4-xynol (0.15 gram), *m*-4-xynol (0.2 gram), *p*-xyloquinol (trace), azoxy-*m*-xylene (5 grams), and *m*-xylidine (odour only). (20a) \* *m*-4-Xylylazide (200 grams), ethyl alcohol (2 volumes), and sulphuric acid (1 volume), after keeping at room temperature and then at 30–35°, gave  $\psi$ -*m*-xyloquinol ethyl ether (14.9 grams), 1:3-dimethylquinol (11.2 grams), *m*-4-xynol (5 grams), *p*-xyloquinol (3.2 grams), *m*-4-xylidine (8 grams), and 2:5-diethoxy-*p*-xylene, but no azoxyxylene. (20'a) \* *m*-4-Xylylazide (110 grams), methyl alcohol (2 volumes), and sulphuric acid (1 volume, 99.9%), after keeping at 12–17° and afterwards at 20–25°, gave 4-imino- $\psi$ -*m*-xyloquinol 1-methyl ether (11 grams), 1:3-dimethylquinol methyl ether (27 grams),  $\psi$ -*m*-xyloquinol (1.4 grams), and *m*-4-xylidine, but no azoxyxylene. (20'a) \* *m*-4-Xylylazide (140 grams), ethyl alcohol (2 volumes), and sulphuric acid (1 volume, 100%), after keeping for eighteen hours at 20°, gave 4-imino- $\psi$ -*m*-xyloquinol 1-ethyl ether (9.2 grams),  $\psi$ -*m*-xyloquinol methyl ether (14 grams),  $\psi$ -*m*-xyloquinol (1.5 grams), *p*-xyloquinol (0.07 gram),

2:5-diethoxy-*p*-xylene (0.35 gram), *m*-4-xylydine (3.1 grams), but no azoxyxylene. (21) (Cf. following abstract.) *m*-4-Xylylhydroxylamine (85 grams) and concentrated hydrochloric acid (saturated at 0°), after keeping for two weeks at 0° gave 5-chloro-*m*-4-xylydine (32 grams), 6-chloro-*m*-4-xylydine (29 grams), and azoxy-*m*-xylene (7 grams). (21a) \* *m*-4-Xylylazide (12 grams) and concentrated hydrochloric acid (saturated at 0°), after keeping for four weeks, gave 5-chloro-*m*-4-xylydine (4.1 grams) and 6-chloro-*m*-4-xylydine (6.4 grams), but no azoxyxylene. (21') (Cf. following abstract.) *m*-4-Xylylhydroxylamine (80 grams) and concentrated hydrobromic acid (saturated at 0°), after seven weeks in the dark, gave 5-bromo-*m*-4-xylydine (45 grams), 6-bromo-*m*-4-xylydine (0.67 gram), *m*-4-xylydine (7.5 grams), and azoxy-*m*-xylene (8.2 grams). (21'a) \* *m*-4-Xylylazide (20 grams) and concentrated hydrobromic acid (saturated at 0°), after two days' keeping, gave 5-bromo-*m*-4-xylydine (17.2 grams), 6-bromo-*m*-4-xylydine (traces), *m*-4-xylydine (1.2 grams), but no azoxyxylene.

An examination of these facts reveals one striking qualitative difference. The production of azoxybenzene derivatives, which is almost always noticed in the transformation of the hydroxylamines, and in some instances occurs to a considerable degree, is never observed in the products of the reactions of the azides. For this reason, the suggestion made by Friedländer and Zeitlin (*loc. cit.*) that their observation of the formation of *o*-nitro-*p*-tolylhydroxylamine from *o*-nitro-*p*-tolylazide by the action of dilute acids is an indication of the general course pursued by the decomposition of the azides, is considered to be extremely improbable.

Apart from the formation of the azoxy-derivatives, there is clearly a close parallelism between the two sets of reactions, from which it is legitimate to argue that a similar mechanism must underlie the two cases. The later stages of the various processes can scarcely be in doubt, and are expressed by the following scheme (illustrative only):





This scheme holds both for hydroxylamines and azides, and the starting points are the quinonoid substances formed by the addition of water, sulphuric acid, methylsulphuric acid, etc., to the arylimide,  $\text{Ar}\cdot\text{N}<$ . No plausible alternative is possible in the cases of the azides, and as on the evidence it is considered that a similar mechanism holds throughout for the azides and hydroxylamines, the latter also must be regarded as being initially broken down into arylimides and water.

In the cases of the hydroxylamines there is, superimposed, the known decomposition into azoxy-compounds and amines.

Although the evidence is strong, it is admitted that no arguments based on the character of the ultimate products can constitute an absolute proof (or disproof) of the mechanism suggested. C. K. I.

**The Behaviour of Arylhydroxylamines towards the Hydrogen Haloid Acids.** EUGEN BAMBERGER (*Annalen*, 1921, **424**, 297–321; cf. preceding abstract).—A large amount of experimental material on the subject is recorded and then submitted to a critical examination in order to unravel the various types of reaction occurring simultaneously.

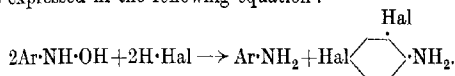
The facts are the following: (1) Phenylhydroxylamine (2 grams) with dilute hydrochloric acid gave *p*-chloroaniline (1.6 grams), azoxybenzene (0.2 gram), a trace of *p*-aminophenol, and probably aniline. For the action of concentrated hydrochloric acid, see preceding abstract. (2) Phenylhydroxylamine with dilute hydrobromic acid gave *p*-bromoaniline (38%), some azoxybenzene, a trace of *p*-aminophenol, and probably some aniline. With concentrated acid, 60 grams of the hydroxylamine gave *p*-bromoaniline (22 grams), *o*-bromoaniline (5.3 grams), *op*-dibromoaniline (2.5 grams), and aniline (4 grams), but no azoxybenzene or aminophenol. (3) Phenylhydroxylamine (3 grams) and dilute hydriodic acid gave azoxybenzene (1.2 grams), aniline (0.6 gram), traces of *p*-aminophenol, and a blue dye. Concentrated acid gave aniline (more than 2 grams from 5) and a blue dye, but no azoxybenzene or aminophenol. (4) Phenylhydroxylamine (4 grams) and saturated hydrofluoric acid, after three weeks' keeping at 0°, gave azoxybenzene (0.1 gram), a volatile base thought to be *p*-fluoroaniline, and an amorphous substance containing fluorine. (5) For the action of concentrated hydrochloric acid on *o*-tolylhydroxylamine, see preceding abstract. Using concentrated hydrobromic acid,

26 grams of the hydroxylamine gave 5-bromo-*o*-toluidide (more than 10 grams), 3:5-dibromo-*o*-toluidine (4.3 grams), *o*-toluidine (more than 0.1 gram), azoxytoluene (1.3 grams crude), and doubtful traces of 6-amino-*m*-cresol. (6) *m*-Tolylhydroxylamine (3 grams) and dilute hydrochloric acid (10 parts of concentrated acid with 40 of water) gave 6-chloro-*m*-toluidine (0.6 gram), azoxy-*m*-toluene (0.5 gram), 5-amino-*o*-cresol (0.8 gram), a violet dye, and some gum. Dilute hydrobromic acid gave (from 3.4 grams of the hydroxylamine) 6-bromo-*m*-toluidine (0.8 gram), 5-amino-*o*-cresol (0.3 gram), and azoxy-*m*-toluene, a violet dye, and some gum. Saturated hydrobromic acid gave (from 4.5 grams of the hydroxylamine) 6-bromo-*m*-toluidine (2.5 grams), and a little azoxy-*m*-toluene. (7) *p*-Tolylhydroxylamine and dilute hydrochloric acid gave much *m*-chloro-*p*-toluidine, some *p*-toluidine, *m*-chloro-*p*-cresol, *p*-azoxytoluene, qualitative traces of *p*-nitrosotoluene, and possibly other products. (8) For the action of hydrochloric and hydrobromic acids on *m*-4-xylylhydroxylamine, see preceding abstract. (9) *p*-Xylylhydroxylamine (13 grams) and concentrated hydrochloric acid gave 5-chloro-*p*-2-xylidine (9.5 grams), 3:5-dichloro-*p*-2-xylidine (traces), and *p*-xylidine (traces). Saturated hydrobromic acid gave (from 11.2 grams of the hydroxylamine), 5-bromo-*p*-2-xylidine (11—12 grams), 3:5-dibromo-*p*-2-xylidine (1—1.5 grams), *p*-xylidine (0.5 gram), and some gum. (10) *p*-Chlorophenylhydroxylamine, m. p. 182° (very approximately), (5.5 grams), and dilute hydrochloric acid gave *op*-dichloroaniline (2.4 grams), *p*-chloroaniline (0.7 gram), *pp'*-dichloroazoxybenzene (1.5 grams), traces of aniline, qualitative traces of *o*-aminophenols and (doubtful) *s*-trichloroaniline. Fuming hydrochloric acid gave (from 7 grams of the hydroxylamine), *op*-dichloroaniline (4 grams), *s*-trichloroaniline (0.45 gram), *p*-chloroaniline (0.8 gram), *pp'*-dichloroazoxybenzene (0.25 gram), a little aniline, and gum. Dry hydrogen chloride in benzene solution gave (from 3.5 grams of the hydroxylamine) *op*-dichloroaniline (1.25 grams), *p*-chloroaniline (0.5 gram), *s*-trichloroaniline (trace), *pp'*-dichloroazoxybenzene, and qualitative traces of *o*-aminophenols. Dilute hydrobromic acid gave (from 5 grams of the hydroxylamine) *p*-chloro-*o*-bromoaniline, *p*-chloroaniline (0.9 gram), a little aniline, and *pp'*-dichloroazoxybenzene (1.6 grams); also qualitative traces of *o*-aminophenols. Saturated hydrobromic acid gave (from 12 grams of the hydroxylamine) *p*-chloro-*o*-bromoaniline (7 grams), *p*-chloro-*oo*-dibromoaniline (3.4 grams), *p*-chloroaniline (2 grams), *pp'*-dichloroazoxybenzene (0.3 gram), and qualitative traces of aniline and of *o*-aminophenols. (11) *p*-Bromophenylhydroxylamine (3 grams) with dilute hydrochloric acid gave *o*-chloro-*p*-bromoaniline (1.3 grams), *p*-bromoaniline (0.3 gram), *pp'*-dibromoazoxybenzene (0.7 gram), and qualitative traces of *o*-aminophenols. Concentrated hydrochloric acid gave (from 11 grams of the hydroxylamine) *o*-chloro-*p*-bromoaniline (5.7 grams), *s*-dichlorobromoaniline (1.9 grams), *p*-bromoaniline (1.7 grams), *pp'*-dibromoazoxybenzene, and qualitative traces of aniline and of *o*-aminophenols. Dilute hydrobromic acid gave (from 6 grams of the hydroxylamine) *op*-dibromoaniline (1.9

grams), *p*-bromoaniline (1 gram), *pp'*-dibromoazoxybenzene (2.3 grams), and an odour of *p*-bromonitrosobenzene (compare 7 above). Concentrated hydrobromic acid gave (from 11 grams of the hydroxylamine) *op*-dibromoaniline (5.7 grams), *s*-tribromoaniline (2.5 grams), and *p*-bromoaniline, besides traces of aniline and of *o*-aminophenols. (12) *p*-Bromophenylhydroxylamine (E. Feilmann, *Diss.*, Basle, 1898) (m. p. 66.5°) gave with dilute hydrochloric acid *p*-chloro-*m*-bromoaniline (m. p. 79.5–80°), an oily chlorobromoaniline (acetyl derivative, m. p. 117–118°), *mm'*-dibromoazoxybenzene, a doubtful trace of *o*-bromo-*p*-aminophenol, some dye, and much gum. With dilute hydrobromic acid the products were a *dibromoaniline* (m. p. 53°), *mm'*-dibromoazoxybenzene (50%), dye, and a trace of *p*-aminophenols.

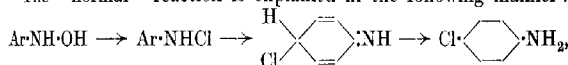
Therefore, four chief types of reaction proceed simultaneously. In the first place, there is what may be termed the "normal" reaction, whereby a single halogen atom enters the ring, in the para-position if possible, in the ortho-position to some extent and particularly if the para-position is occupied, or in the meta-position, if, for instance, most of the other usual positions are occupied :

$\text{Ar}\cdot\text{NH}\cdot\text{OH} + \text{H}\cdot\text{Hal} \rightarrow \langle \text{Hal} \rangle \cdot \text{NH}_2$ . The second type of reaction is that expressed in the following equation :



This is termed the "abnormal" reaction. In addition, the hydroxylamines decompose into azoxy-compounds and amines, or by atmospheric oxidation into azoxy-compounds, or again by reduction (for example, by means of hydriodic acid) into amines. Finally, there is the type of decomposition due to the action of hydrogen ions and dealt with in the preceding abstract.

The "normal" reaction is explained in the following manner :



or by a similar mechanism involving an *o*-quinonoid intermediate product. The production of derivatives of *m*-chloroaniline is then easily explained by assuming addition of the halogen hydride to one of the double bonds of the quinonoid structure. The abnormal reaction also is discussed in the light of cognate reactions, but no entirely satisfactory solution is arrived at. C. K. I.

**The Complete and Partial Reduction of Nitro-compounds with Iron.** H. POMERANZ (*Chem. Zeit.*, 1921, 45, 866–867).—When picric acid is reduced with iron and a large excess of hydrochloric acid in a similar manner to that used for 2 : 4-dinitrophenol (D.R.-P. 269542, A., 1914, i, 948) a blue-black powder is obtained as a result of the oxidation of triaminophenol. In this instance, the excess of hydrochloric acid does not protect the triamine owing to the rapid oxidation of ferrous chloride by unreduced picric acid.



On the other hand, picramic acid is neatly reduced to triaminophenol by this process. Picramic acid is usually prepared by reducing picric acid with sodium sulphide, but it may be obtained more cheaply by the use of iron and sulphurous acid (D.R.-P. 289454, A., 1916, i, 382). Picric acid is only slightly soluble in water, but when heated with water and iron it dissolves, probably as an iron salt. The prolonged passage of sulphur dioxide through such a solution results in rise of temperature and picramic acid separates. The yield is practically theoretical and the product is sufficiently pure for technical purposes.

F. M. R.

#### Electrolytic Reactions of Naphthalene and its Derivatives.

**II. Electrolytic Oxidation of  $\alpha$ -Naphthol.** KASHICHI OXO (*J. Chem. Soc. Japan*, 1921, 42, 559—578; cf. this vol., i, 334).—By the electrolytic oxidation of  $\alpha$ -naphthol in acid solution,  $\alpha$ -naphthaquinone, a compound of  $\alpha$ -naphthol and  $\alpha$ -naphthaquinone (*Ber.*, 1909, 42, 1153), phthalic acid, and a dark violet compound are obtained in the anode chamber, whilst a red compound is produced in the cathode chamber. The dark violet compound, having a phenolic hydroxyl group, gave phthalic and phthalonic acids by oxidising with potassium permanganate, phthalic acid by fusing with potassium hydroxide, and naphthalene and  $\alpha$ -dinaphthol by distilling with zinc dust. The author gives optimum conditions for the operation. The electrolytic oxidation of  $\alpha$ -dinaphthol and  $\alpha$ -naphthol- $\alpha$ -naphthaquinone to  $\alpha$ -naphthaquinone, and to  $\alpha$ -naphthaquinone and phthalic acid respectively, is described (cf. *J. Soc. Chem. Ind.*, 1921, Oct.).

K. K.

**Allyl Derivatives of Resorcinol and Quinol.** F. MAUTHNER (*J. pr. Chem.*, 1921, 102, 41—44).—The preparation and intramolecular transformation of allyl derivatives of phenols have been described by Claisen (A., 1913, i, 1175; 1919, i, 266) and the reactions have been used by the author (A., 1917, i, 544, and following abstract) in his investigations of plant substances. The behaviour of monomethylresorcinol and monomethylquinol has now been investigated.

Monomethylresorcinol dissolved in acetone is converted by allyl bromide in the presence of powdered potassium carbonate into 2-methoxyphenyl allyl ether, a colourless liquid, b. p. 125—126°/15 mm., which is transformed when heated with dimethylaniline into 2-hydroxy-4-methoxyallylbenzene, b. p. 143—144°/15 mm. The constitution of the latter substance is deduced from its complete methylation to 2:4-dimethoxyallylbenzene, a colourless liquid, b. p. 125—126°/14 mm., which is oxidised by potassium permanganate to dimethyl- $\beta$ -resoreic acid, m. p. 108°. 4-Methoxyphenyl allyl ether, b. p. 119—120°/13 mm., is transformed in the presence of boiling dimethylaniline into 6-hydroxy-3-methoxyallylbenzene, a colourless liquid, b. p. 144—145°/13 mm., which is converted by methyl sulphate into 3:6-dimethoxyallylbenzene, a colourless liquid, b. p. 126°/14 mm.

H. W.

**Synthesis of Pikamar.** F. MAUTHNER (*J. pr. Chem.*, 1921, 102, 36—40).—Pikamar was isolated in 1833 by Reichenbach

from beechwood tar and examined subsequently by Hofmann (A., 1880, 248), Niederrist (*Monatsh.*, 1883, 4, 487), and Will (A., 1888, 1089). The work of these chemists has sufficed to elucidate the constitution of the substance, but has not shown whether a propyl or an isopropyl group is present. The author has therefore synthesised 4-hydroxy-3:5-dimethoxy-*n*-propylbenzene, which is shown to be identical with pikamar.

2:6-Dimethoxyphenyl allyl ether (Mauthner, A., 1918, i, 428) is converted by being heated with dimethylaniline (compare Claisen, A., 1913, i, 1175) into 4-hydroxy-3:5-dimethoxyallylbenzene, which is transformed by acetyl chloride and glacial acetic acid into 4-acetoxy-3:5-dimethoxyallylbenzene, m. p. 43–44°. The latter is reduced by hydrogen in the presence of colloidal palladium to 4-acetoxy-3:5-dimethoxypropylbenzene, m. p. 87° (cf. Hofmann, *loc. cit.*), which, when hydrolysed, gives 4-hydroxy-3:5-dimethoxy-*n*-propylbenzene, b. p. 285°. H. W.

**Synthesis and Dehydration of Phenylethylpropylcarbinol** [ $\gamma$ -Phenylhexan- $\gamma$ -ol]. VARTKES YÉRAMIAN (*Compt. rend.*, 1921, 173, 362–364).—Propyl phenyl ketone reacts readily with magnesium ethyl bromide to give  $\gamma$ -phenylhexan- $\gamma$ -ol, b. p. 132°/25 mm., which, when dehydrated by passing its vapour over infusorial earth at a red heat, gives  $\gamma$ -phenyl- $\Delta^2$ -hexene, b. p. 216°. W. G.

**Esters of Aminobenzoic Acids.** HARVEY C. BRILL (*J. Amer. Chem. Soc.*, 1921, 43, 1320–1323).—Certain esters of the aminobenzoic acids have been prepared by reduction of the corresponding nitrobenzoic esters, with the view of studying their anæsthetic properties. The following compounds are described. *Allyl p-nitrobenzoate*, a liquid, allyl *p*-aminobenzoate, m. p. 52°, giving a *hydrochloride*, m. p. 180°; *isopropyl p-nitrobenzoate*, m. p. 95°, *sopropyl p-nitrobenzoate*, m. p. 79°, and its *hydrochloride*, m. p. 184°; *n-butyl p-nitrobenzoate*, m. p. 35°, *n-butyl p-aminobenzoate*, m. p. 58°, and its *hydrochloride*, m. p. 198°; *n-butyl m-nitrobenzoate*, liquid, *n-butyl m-aminobenzoate*, and its *hydrochloride*, m. p. 128°; *n-butyl o-nitrobenzoate*, a liquid, and its *hydrochloride*, m. p. 178°; *ethyl 3:5-dinitrobenzoate*, m. p. 91°, *ethyl 3:5-diaminobenzoate*, m. p. 84°, and its *hydrochloride*, m. p. 248°; *n-butyl 2:4-dinitrobenzoate*, m. p. 70°, *n-butyl 2:4-diaminobenzoate*, m. p. 90°, and its *hydrochloride*, m. p. 270°; *n-butyl 3:5-dinitrobenzoate*, m. p. 61°, *n-butyl 3:5-diaminobenzoate*, and its *hydrochloride*, m. p. 253°.

A rough test of anæsthetic properties showed that *n*-butyl, allyl, and *isopropyl p*-aminobenzoates and *n*-butyl 3:5-diaminobenzoate were the most active and *n*-butyl 2:4-diaminobenzoate the least active as local anæsthetics. W. G.

**The *o*-Diethylaminocyclohexanylester of *p*-Aminobenzoic Acid.** A. E. ØSTERBERG and E. C. KENDALL (*J. Amer. Chem. Soc.*, 1921, 43, 1370–1371).—*o*-Chlorocyclohexanol reacts with diethylamine to yield *o*-diethylaminocyclohexanol, b. p. 224°/730 mm., giving a *hydrochloride*, m. p. 160°. The alcohol condenses with

*p*-nitrobenzoyl chloride to give *o*-diethylaminocyclohexan-1-yl *p*-nitrobenzoate, giving a hydrochloride, m. p. 175°, which on reduction with tin and hydrochloric acid gives *o*-diethylaminocyclohexan-1-yl *p*-aminobenzoate, m. p. 72°, and its hydrochloride, m. p. 163°. The physiological action of this ester is being studied. W. G.

**Condensation of Nitriles and Thioamides. I. Benzonitrile and Thiobenzamide.** SEIICHI ISHIKAWA (*J. Chem. Soc. Japan*, 1921, 42, 579—586).—Matsui (*Mem. Coll. Sci. Eng. Kyoto*, 1910, 2, 401) isolated a condensation product of benzonitrile and thiobenzamide, and considered it to be benziminosulphide,  $\text{S}(\text{CPh}:\text{NH})_2$ . The author oxidised the condensation product with 0.1*N*-iodine in alcoholic solution, and found that the quantity of iodine used, the nature of the resulting product, and the non-evolution of hydrogen sulphide do not support this view. By reducing the substance with zinc dust and hydrochloric acid in alcoholic solution, benzylbenzamidine was isolated, accompanied by the evolution of hydrogen sulphide, indicating the presence of the groups  $-\text{C}(\text{N})\text{N}:\text{C}-$  and  $-\text{SH}$ . Moreover, by alkylation with ethyl iodide, it gave ethyl benziminoisothiobenzamide hydriodide, yellow, monoclinic crystals, m. p. 181°, the ethyl group combining with the sulphur atom. The condensation would therefore appear to proceed as follows, producing benziminoisothiobenzamide:  $\text{SH}\cdot\text{CPh}:\text{NH} + \text{PhCN} = \text{SH}\cdot\text{CPh}:\text{N}\cdot\text{CPh}:\text{NH}$ . K. K.

**The Nitro- and Amino-derivatives of *m*-Hydroxybenzoic Acid.** VICTOR FROELICHER and JULIUS BEREND COHEN (*T.*, 1921, 119, 1425—1432).

**The Additive Properties of the Keto-enolic Double Linking.** H. GAULT and R. WEICK (*Compt. rend.*, 1921, 173, 391—393).—Ethyl phenylpyruvate reacts with acid anhydrides and acid chlorides, giving the corresponding esters. Thus with acetic anhydride the  $\beta$ -ester gives ethyl  $\alpha$ -acetoxycinnamate,  $\text{CHPh}:\text{C} \begin{smallmatrix} \text{CO}_2\text{Et} \\ \text{OAc} \end{smallmatrix}$ , m. p. 33—34°, and with benzoyl chloride the corresponding benzoyloxy-derivative, m. p. 87°. These two derivatives do not form additive compounds with bromine, but always yield substituted compounds. The presence of the double linking is verified by the fact that they immediately decolorise potassium permanganate in alkaline solution. Dilute potassium hydroxide solution rapidly regenerates ethyl phenylpyruvate from these two derivatives. W. G.

**Resolution of *dl*-*trans*-cyclopentane-1 : 3-dicarboxylic Acid.** WILLIAM HENRY PERKIN, jun., and HAROLD ARCHIBALD SCARBOROUGH (*T.*, 1921, 119, 1400—1408).

**The Dinaphthanthracene Series. IV. Bromo-derivatives.** ERNST PHILIPPI and FEDORA AUSLAENDER (*Monatsh.*, 1921, 42, 1—4; cf. A., 1911, i, 793; 1913, i, 627; 1914, i, 826; Mills and Mills, *T.*, 1912, 101, 2194).—Pyromellitic anhydride condenses with bromobenzene in the presence of aluminium chloride to yield a mixture of 2 : 5-di-*p*-bromobenzoyltetraphthalic acid, m. p. 306—

309° (decomp.) and 4:6-di-p-bromobenzoylisophthalic acid, m. p. 256—260° after previous decomposition, which are separated by crystallisation from glacial acetic acid; by analogy with the dibenzoylphthalic acids, the substance of higher melting point is considered to have the carboxyl groups in the para-position to one another. The acids lose water when heated with concentrated sulphuric acid, giving 2:9-dibromo-5:7:12:14-dinaphthanthradiquinone, greenish- or brownish-yellow needles, which gradually darken and decompose above 250°, and 2:10-dibromo-5:7:12:14-dinaphthanthradiquinone respectively. H. W.

**New Method for the Preparation of Mellitic Acid.** ERNST PHILIPPI and GERTRUD RIE (*Monatsh.*, 1921, 42, 5—8).—1:3:5-trimethyl-2:4-diethylbenzene, a colourless liquid, b. p. 229—236° is obtained by the reduction of diacetylmesitylene with amalgamated zinc and hydrochloric acid; it is converted by acetyl and aluminium chlorides in the presence of carbon disulphide into 6-acetyl-1:3:5-trimethyl-2:4-diethylbenzene, a pale yellow liquid with a powerful odour of violet root, b. p. 286—304°, which is reduced to 1:3:5-trimethyl-2:4:6-triethylbenzene, a colourless liquid, b. p. 238—247°. The acetyl compound is oxidised by nitric acid to mellitic acid, m. p. 285—286°. H. W.

**Constitution of the Bile Acids.** W. BORSCHKE (*Nachr. Ges. Wiss. Göttingen*, 1920, 188—194; from *Chem. Zentr.*, 1921, iii, 74. Cf. A., 1919, i, 276, 476).—[With HERBERT BEHR.]—*iso-α-cholanetricarboxylic acid*, obtained by reduction of *isobilianic acid* with zinc and hydrochloric acid in glacial acetic acid solution, gives colourless needles, m. p. 261° (decomp.). The trimethyl ester,  $C_{27}H_{44}O_6$ , forms lustrous leaflets, m. p. 103—104°.

[With HANS WIECKHORST.]—*Ethyl dihydrogen β-cholanonetricarboxylate*,  $C_{26}H_{40}O_7$ , gives long, white needles, m. p. 136°. The monomethyl ester has m. p. 247°. The oxime,  $C_{24}H_{37}O_7N$ , forms transparent crystals, m. p. 227°. By heating with 90% sulphuric acid an isomeric *oximic acid* is obtained by rearrangement, giving stout, lustrous crystals decomposing at 273—274°. *β-Cholanedionecarboxylic acid diorime*,  $C_{24}H_{38}O_4N_2$ , sinters at 250° and decomposes at 273°. The *isoorime* has m. p. 164°. The acid has m. p. 274—275°. It is prepared by the reduction of *β-cholanetricarboxylic acid*. By distillation of *β-cholanetricarboxylic acid* in a vacuum, a distillate is obtained from which, after repeated recrystallisation from acetic acid, a substance is obtained, m. p. 205—207°. From mono-ethyl *β-cholanetricarboxylate*, the anhydride,  $C_{26}H_{38}O_6$ , is obtained by distillation. G. W. R.

**Preparation of Hydroxyaryl Aldehydes.** HERMANN HAAKH (*Brit. Pat.* 157850).—Hydroxyaryl aldehydes are obtained by reacting phenols with formaldehyde in presence of a nitroso-compound and an acid condensing agent. An azo-methine is formed intermediately, and decomposes into aldehyde and amine. For example, 60 grams of guaiacol and 109 grams of nitrosodiethyl-aniline hydrochloride (or the corresponding amount of nitroso-phenol), dissolved in 500 grams of methyl alcohol, are saturated

with hydrogen chloride and boiled in a reflux apparatus. Seventy grams of 23% formaldehyde solution are slowly added, and when the reaction is complete the alcohol is distilled off. From the residue, after boiling for a short time in feebly alkaline solution followed by re-acidification, the vanillin is extracted with ether and purified in the usual way.

G. F. M.

**The Allylcyclohexanones and the Methylallylcyclohexanones.** R. CORNUBERT (*Ann. Chim.*, 1921, [ix], **16**, 141—220).—

A more detailed account of work already published (cf. A., 1914, i, 951, 969; 1920, i, 390, 485; this vol., i, 422; ii, 5).

W. G.

#### Action of Nitroso-derivatives on Unsaturated Compounds.

L. ALESSANDRI (*Gazzetta*, 1921, **51**, ii, 129—144).—A fuller account is given of work already published (A., 1915, i, 555).

The action of nitrosobenzene on estragole in the dark yields the compound,  $C_{16}H_{15}O_2N$ , which forms stellar aggregates of golden-yellow, prismatic needles, m. p.  $165^\circ$ . Nitrosobenzene and methyl-eugenol give the compound,  $C_{17}H_{17}O_2N$ , in stellar aggregates of highly refractive, yellow prisms, m. p.  $154^\circ$ , decomposing rapidly in direct sunlight, and nitrosobenzene and myristicin, the compound,  $C_{17}H_{15}O_4N$ , which forms groups of deep yellow scales, m. p.  $180^\circ$ , and is decomposed gradually by diffused, and rapidly in direct, sunlight.

In addition to the products named (*loc. cit.*), azoxybenzene is formed by the action of nitrosobenzene on parsley-apiole.

The action of nitrosobenzene on isosafrole does not give the N-phenyl derivative of piperonaldoxime, as would be expected from the course followed by the interaction of nitrosobenzene and asarone (*loc. cit.*), but is accompanied by secondary oxidation and reduction, piperonaldehyde being detectable among the products, together with a substance yielding aniline when boiled with dilute acid.

T. H. P.

**Unsaturated Compounds. III. Condensation of *p*-Aminoacetophenone and Acetyl-*p*-aminoacetophenone with Aromatic Aldehydes.** M. GIUA and E. BAGIELLA (*Gazzetta*, 1921, **51**, ii, 116—125; cf. A., 1920, i, 676).—By the condensation of *p*-aminoacetophenone or its acetyl derivative with various aromatic aldehydes in alcoholic solution containing sodium or potassium hydroxide, unsaturated ketones have been obtained (cf. Scholtz and Huber, A., 1904, i, 253). These have been treated with bromine in order to ascertain if the presence in the aromatic ring of the group  $-NHR$  influences in any particular way the manner in which the halogen is added to the double linking.

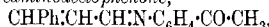
*p*-Benzylideneaminoacetophenone and the compound, m. p.  $143^\circ$ , prepared from *p*-aminoacetophenone and benzaldehyde in alcoholic solution containing sodium hydroxide, have been already described by Scholtz and Huber (*loc. cit.*). The action of bromine on the compound, m. p.  $143^\circ$ , yields: (1) a compound,  $C_{22}H_{17}ONBr$ , m. p.  $145^\circ$  (crude), and (2) a pale yellow, amorphous compound, m. p.  $209^\circ$ , containing 59.67% of bromine.

*p*-Anisylideneaminoacetophenone,  $OMe \cdot C_6H_4 \cdot CH : N \cdot C_6H_4 \cdot CO \cdot CH_3$

forms silvery needles, m. p. 124—125°, and gives an intense orange-yellow coloration with concentrated sulphuric acid.

The compound,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH:N}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH:CH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , crystallises in yellow lamellæ, m. p. 149—150°, and, like the compound, m. p. 191°, obtained by Scholtz and Huber from anisaldehyde and *p*-aminoacetophenone, forms a purple coloration with concentrated sulphuric acid. The action of bromine in chloroform solution on the compound, m. p. 149—150°, gives a pale orange, amorphous compound containing 43.98% of bromine, the latter replacing hydrogen atoms of the aromatic nuclei as well as saturating the double linking.

*p*-Cinnamylideneaminoacetophenone,

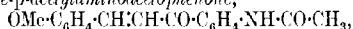


forms lustrous, pale yellow plates, m. p. 126—127°.

The compound,  $\text{CHPh}\cdot\text{CH:CH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH:CH}\cdot\text{CHPh}$ , obtained from cinnamaldehyde and *p*-aminoacetophenone, forms golden-yellow needles, m. p. 162—163°, and gives a reddish-violet coloration with concentrated sulphuric acid. The compound, m. p. 191°, to which Scholtz and Huber ascribed this structure, is probably the result of more advanced condensation. The *hexabromide*,  $\text{CHPhBr}\cdot\text{CHBr}\cdot\text{CH:N}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{CHPhBr}$ , is a deep yellow, amorphous compound, m. p. 192° (decomp.).

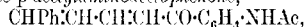
Benzylidene-*p*-acetylaminoacetophenone, obtained from *p*-acetylaminoacetophenone and benzaldehyde, forms yellow crystals, m. p. 168°, and gives a reddish-yellow coloration with concentrated sulphuric acid; Rupe and Porai-Koschitz (A., 1906, i, 754) gave m. p. 179°. Its *dibromide*,  $\text{CHPhBr}\cdot\text{CHBr}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_3$ , crystallises in pale yellow prisms, m. p. 175°.

*Anisylidene-p*-acetylaminoacetophenone,



crystallises in yellow lamellæ, m. p. 198°, and forms a red, oily, dibromide, which could not be purified.

*Cinnamylidene-p*-acetylaminoacetophenone,



forms yellow crystals, m. p. 183—184°, reddens rapidly when left moist in the air, and gives a brick-red coloration with concentrated sulphuric acid. Its *tetrabromide*,  $\text{C}_{19}\text{H}_{17}\text{O}_2\text{NBr}_4$ , crystallises in white needles, m. p. 195° (decomp.).

In chloroform or benzene solution, cinnamylideneacetophenone is converted by the action of light into a dimeric modification which, when heated, undergoes transformation into the monomeric, *isocinnamylideneacetophenone* (Stobbe and Rücker, A., 1911, i, 385). Attempts to prepare, in a similar way, the dimeride of cinnamylidene-*p*-acetylaminoacetophenone have proved unsuccessful.

T. H. P.

**The Influence of Steric Factors on Intramolecular Condensation.** JAMES KENNER and ERNEST WITAM (T., 1921, 119, 452—4461).

**Crystalline Form of Trimethylphloreitin.** MARIA DE ANGELIS *Atti R. Accad. Lincei*, 1921, [v], 30, i, 348—351).—This com-

pound,  $C_6H_5O_2Me_3CO\cdot CHMe\cdot C_6H_4\cdot OH$  (compare Ciamician and Silber, A., 1895, i, 538), forms crystals belonging to the prismatic class of the monoclinic system,  $a : b : c = 0.4505 : 1 : 0.3410$ ,  $\beta = 71^\circ 13'$ ;  $d = 1.306$ .  
T. H. P.

**Migration of the Sulphonic Acid Group in Aromatic Molecules.** JH. MARTINET (*Rev. gén. Mat. colorantes*, 1921, 25, 49—51; from *Chem. Zentr.*, 1921, iii, 224—225).—The sulphonation of anthraquinone takes place first in the  $\alpha$ -position and then in the  $\beta$ -position. The formation of the  $\beta$ -sulphonic acid is due to transformation from the  $\alpha$ -acid. In the absence of other substances, the sulphonation of anthraquinone requires a fairly high temperature, and under such conditions the rate of transformation of the  $\alpha$ - into the  $\beta$ -sulphonic acid is of the same order as the formation of the  $\alpha$ -acid, with the result that only the  $\beta$ -acid is obtained. In order to obtain the  $\alpha$ -acid, it is necessary to employ a catalyst which lowers the temperature of sulphonation without influencing the rate of transformation of the  $\alpha$ - into the  $\beta$ -acid. By the use of mercury in this way as a catalyst, the  $\alpha$ -sulphonic acid can be obtained at a lower temperature. That this explanation is correct was shown (in collaboration with A. Roux) by the fact that the  $\alpha$ -sulphonic acid thus prepared is transformed into the  $\beta$ -acid at a higher temperature. The transformation also takes place even in the presence of mercury with suitable conditions of temperature and concentration. In order to obtain the 1:5-disulphonic acid, the reaction must take place at a higher temperature, and more sulphur trioxide must be used.  
G. W. R.

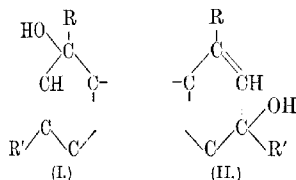
**Some Derivatives of Anthraquinonedi-imide.** LEON PIERRE GEORGE KEFFLER (T., 1921, 119, 1476—1482).

**Sesquiterpene Groups. II. Machilol and Atractylol.** SEIJI TAKAGI (*J. Pharm. Soc. Japan*, 1921, No. 473, 565—587).—By distilling Formosan *Machilus Kusanoi*, Hayata (Lauraceæ), in steam, a light yellow, viscous oil was obtained. The fraction 140—170°/5 mm. was recrystallised from dilute alcohol and sublimed in a vacuum, yielding a new sesquiterpene alcohol, *machilol*,  $C_{15}H_{26}O$ , white needles, m. p. 79—80°, b. p. 160°/14 mm.,  $[\alpha]_D^{20} + 30.08^\circ$  in alcohol. The alcohol decolorises potassium permanganate and bromine solutions, but does not form an ester or phenylurethane. By reducing with hydrogen in the presence of platinum black in alcoholic solution, the alcohol gave *dihydromachilol*,  $C_{15}H_{28}O$ , m. p. 82—83°, b. p. 157—158°/14 mm.,  $[\alpha]_D^{20} + 16.43^\circ$  in alcohol. By heating with formic acid, *machilol* yields *machilene*,  $C_{15}H_{24}$ , a colourless oil,  $d_4^{25} = 0.9109$ ,  $[\alpha]_D^{25} + 58.73$ ,  $n_D^{25} = 1.51257$ , by losing one molecular proportion of water. The product is, however, apparently a mixture of two isomerides, since the specific rotation of the product is not constant, but varies according to the time and temperature of heating with formic acid. *Machilene* yields *tetrahydromachilene*, a colourless, mobile oil, b. p. 132°/11 mm.,  $d_4^{20} = 0.8964$ ,  $[\alpha]_D^{20} + 37.04^\circ$ ,  $n_D^{20} = 1.48645$ , by reducing with hydrogen in glacial acetic acid solution, using platinum black as catalyst.

By oxidation with dilute potassium permanganate in benzene solution, machilol gave *dihydroxymachilol*,  $C_{11}H_{26}O(OH)_2 \cdot H_2O$ , white needles, m. p.  $110^\circ$  (*anhydride*, m. p.  $107-108^\circ$ ), which gave a *monobenzoate*, white, square plates, m. p.  $142^\circ$ , by the Schotten-Baumann method.

Gadamer and Amenomiya (A., 1903, i, 353), described atractylol as possessing no rotatory power, whilst the author found that a sample of the compound isolated from *Atractylis ovata*, [Thunb., had  $[\alpha]_D^{25} -17.1^\circ$  in alcoholic solution. The same sample gave *dihydroatractylol*, a colourless, viscous oil, b. p.  $156-158^\circ/4$  mm.,  $[\alpha]_D^{25} +14.9^\circ$ , by reducing with hydrogen in glacial acetic acid solution in the presence of platinum black; and *atractylene* perhaps a mixture of two isomerides, a colourless oil, b. p.  $108-109^\circ/3$  mm.,  $d_4^{25} 0.9189$ ,  $[\alpha]_D^{25} +78.25^\circ$ ,  $n_D^{25} 1.51795$ , by heating with formic acid. Atractylene yields *tetrahydroatractylene*, a colourless, mobile oil, b. p.  $129-130^\circ/10$  mm.,  $d_4^{25} 0.9030$ ,  $[\alpha]_D^{25} +36.99^\circ$ ,  $n_D^{25} 1.49589$ , by reducing with hydrogen in the presence of platinum black. On treatment by the same method as was used in the oxidation of machilol, atractylol gave  *$\alpha$ -dihydroxyatractylol*,  $C_{11}H_{26}O(OH)_2 \cdot H_2O$ , needles, m. p.  $110^\circ$  (*anhydride*, m. p.  $107-108^\circ$ ),  $[\alpha]_D^{25} -25.34^\circ$ , and a small quantity of the  $\beta$ -isomeride, needles, m. p. about  $78^\circ$ ,  $[\alpha]_D^{25} +24.68^\circ$ . Both  $\alpha$ - and  $\beta$ -compounds produced a *monobenzoate*, square plates, m. p.  $142^\circ$ , by the Schotten-

Baumann method. Thus dihydroxy- and tetrahydro-machilol are identical with dihydroxy- and tetrahydro-atractylol respectively. Machilol (annexed formula I) and atractylol (II) and the corresponding hydrocarbons have therefore the



same constitutional skeleton, differing in the positions of the double bonds and the hydroxyl group.

K. K.

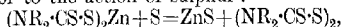
**Swelling of Caoutchouc in Various Liquids.** WOLFGANG OSTWALD (*Kolloid Zeitsch.*, 1921, 29, 100-105).—A theoretical paper in which an attempt is made to establish a connexion between the swelling power of a substance and some definite physical property of the liquid which effects the swelling. The previously published results of Flusin (A., 1908, ii, 359) and Posnjak (A., 1912, ii, 912) on the swelling of caoutchouc in a series of liquids have been used. As a first approximation, it is shown that the swelling power decreases with increasing dielectric constant of the liquid. This is expressed by the equation  $\sqrt[3]{Q} \cdot D = K$ , in which  $Q$  is the swelling power,  $D$  the dielectric constant,  $K$  a constant, and  $n$  a number between 2 and 3. If  $n$  is chosen as 2.16, the mean value of  $K$  for 4 solvents ( $D=2.3-81$ ) is 50, with extreme values of 74 and 29. These variations are regarded as accidental, and due in part to exact values of the dielectric constant. It is shown that swelling power and solubility cannot be directly compared, but swelling



power and the reciprocal of the solubility (Lösungsmittelbedarf) may. The similarity of the above relationship to the Walden relationship between the solubility and the dielectric constant,  $D = \sqrt{\mu \cdot K}$ , is pointed out and discussed. J. F. S.

**Mechanism of the Action of certain Accelerants of the Vulcanisation of Caoutchouc.** G. BRUNI and E. ROMANI (*Atti R. Accad. Lincei*, 1921, [v], 30, i, 337—344).—It has been commonly assumed that accelerators of vulcanisation are substances capable of reacting with the added sulphur to form polysulphides, which then yield their sulphur with liberation of the original accelerating compounds. This hypothesis has been advanced in various forms by Östromisslenski (A., 1916, i, 277), Kratz, Flower, and Coolidge (*J. Ind. Eng. Chem.*, 1920, 12, 317), and Bedford and Scott (*J. Ind. Eng. Chem.*, 1920, 12, 31). Most probably true is the view of the last of these authors, who distinguish between the two types of accelerators: (1) Bases forming polysulphides similar to yellow ammonium sulphide, and (2) thiocarbamides, dithiocarbamates, thiourams, mercaptans, and the disulphides formed from them by oxidation or by reaction with sulphur. To the latter group, which alone contains accelerators sufficiently active to be termed ultra-accelerators, must be added alkylxanthates (cf. this vol., i, 575).

Thiouram disulphides are obtainable by the oxidation of dithiocarbamates of imines or by subjecting metallic dithiocarbamates to oxidation or to the action of sulphur:



and this equation represents the manner in which zinc alkyl- and aryl-dithiocarbamates act in the caoutchouc-sulphur mixture. Similarly, zinc alkylxanthates are able to function as ultra-accelerators, since they readily undergo oxidation to form disulphides,  $(\text{NR}_2 \cdot \text{CS})_2 \text{S}_2$ , which are perfectly analogous to those of the thiourams, the so-called dioxanthogens,  $(\text{OR} \cdot \text{CS})_2 \text{S}_2$ . It is thus definitely shown that the presence of nitrogen and the possession of basic properties are quite unnecessary in an accelerator.

Ultra-accelerating effects are exerted in presence of metallic oxides also by the thiolbenzthiazoles, for instance,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{S} \end{smallmatrix} \text{C} \cdot \text{SH}$ ,

and by the disulphides they yield on oxidation  $(\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{S} \end{smallmatrix} \text{C})_2 \text{S}_2$ . Since thiolbenzthiazole may be obtained in good yield by the action of sulphur on methylenedianiline (anhydroformaldehyde-aniline), the cause of its accelerating action of the latter is evident.

Trisubstituted thiocarbamides are able to yield thiocarbamides,  $\text{NHAr} \cdot \text{CS} \cdot \text{NR}_2 \rightarrow \text{NAr} \cdot \text{CS} + \text{NHR}_2$ , and thus act as accelerators in the same way as the above compounds. On the other hand, tetra-substituted thiocarbamides, which do not undergo this reaction, are totally devoid of accelerating properties.

The function of zinc oxide in favouring acceleration consists in the formation of the zinc salts of the thio-acids, these by the action of free sulphur losing the zinc as zinc sulphide and yielding the organic disulphides which are the true accelerators. T. H. P.

**Sols and Gels of Vulcanised Caoutchouc.** HENRY P. STEVENS (*J. Soc. Chem. Ind.*, 1921, 40, 186t—190t).—Although vulcanised caoutchouc does not dissolve in the ordinary solvents, solutions of vulcanised caoutchouc can be obtained by heating solutions of raw caoutchouc with sulphur to the customary vulcanising temperatures. With xylene or toluene as solvent, combination of rubber with sulphur proceeds more rapidly than when benzene is used; with a 10% solution of a mixture of caoutchouc and sulphur (90:10) in this solvent, the rate of combination is about half that with the dry mixture at the same temperature. Vulcanisation of a dilute solution does not cause any great change in viscosity. Solutions of vulcanised caoutchouc prepared in this manner, on evaporation, yield films which refuse to redissolve in the solvent. If the solutions are too concentrated or if vulcanisation progresses too far, gelation occurs. Similar behaviour is observable in the vulcanisation of dissolved caoutchouc with sulphur chloride at the ordinary temperature. Vulcanisation in solution can also be effected, with the aid of heat, by trinitrobenzene in the presence of litharge. On exposure to light, the solutions of caoutchouc vulcanised with sulphur or sulphur chloride gelatinise, the effect being reversible in the dark; prolonged exposure to light may cause the primarily produced gels to liquefy owing to degradation of the caoutchouc. D. F. T.

**Phenolcoumारेin and Resorcinolcoumारेin.** SRI KRISHNA (T., 1921, 119, 1420—1425).

**Arylated Pyridines and their Relationships to the Corresponding Pyrylium Compounds. II.** WALTHER DILTHEY [with G. BAURIEDER, B. BURGER, G. GEISSELBRECHT, F. VON IRACH, F. KIEFER, A. SEEGER, O. SIMON, R. TAUCHER, and J. WINKLER] (*J. pr. Chem.*, 1921, 102, 209—240; cf. A., 1920, i, 448).—Arylpyridines are readily accessible, since it has been found that purely aromatic pyrylium salts and their *pseudo*-bases, like the corresponding aliphatic derivatives (cf. Baeyer and Piccard, A., 1911, i, 901) are readily converted by ammonia into arylpyridines. The yields are quantitative when the pyrylium iron salt is decomposed in a medium in which the pyridine produced is soluble. With increases in the number of phenyl groups present in the molecule, the basicity of the phenylated pyridine diminishes, or, at any rate, the stability of the salts towards water becomes less. Simultaneously, the addition of methyl iodide becomes more difficult. This behaviour is in striking contrast with the existence of tetra- and penta-phenylated pyrylium salts and is regarded by the author as further confirmation of his formulation of pyrylium salts in which the acid radicle is regarded as attached to the whole of the remainder of the molecule instead of to a specific atom. A further point of contrast between pyrylium and pyridine compounds is afforded by the ready convertibility of the former into quinopyran derivatives, whereas the latter do not appear to be able to yield similar compounds. In accordance with the conceptions of Lautensch (A., 1920, i, 34) the salts of the arylpyridines are regarded

as non-ionised additive compounds. Such as have been analysed contain acid and base in molecular proportions, but indications are not lacking that union can also occur with more than one molecular proportion of acid, the effect being hypsochromic.

The following individual compounds are described: 4-phenyl-2:6-di-p-chlorophenylpyridine (from a suspension of the 4-phenyl-2:6-di-p-chlorophenylpyrylium iron salt and ammonia), slender, colourless needles, m. p.  $183^{\circ}$  (hydrochloride, m. p. about  $250^{\circ}$ ; picrate, lemon-yellow needles, m. p.  $236^{\circ}$ ); 4:6-di-phenyl-2-p-naphthylpyridine, almost colourless needles, m. p.  $124-123^{\circ}$  (picrate, yellow needles, m. p.  $233-234^{\circ}$ ); 4-phenyl-2:6-di-p-tolylpyridine, almost colourless crystals, m. p.  $158-159^{\circ}$  (hydrochloride, nitrate; picrate, pale yellow needles, m. p.  $222^{\circ}$ ); 2:4-diphenyl-6-p-tolylpyridine, almost colourless, lustrous leaflets, m. p.  $121^{\circ}$  (hydrochloride, indefinite m. p., picrate, pale yellow prisms, m. p.  $192^{\circ}$ ); 4:6-di-phenyl-2-p-diphenylpyridine, almost colourless needles, m. p.  $141^{\circ}$  (chloride, decomp. about  $130^{\circ}$ ; picrate, yellow prisms, m. p.  $180^{\circ}$ ); 2:6-di-phenyl-4-p-anisylpyridine, lustrous leaflets, m. p.  $100-101^{\circ}$  (picrate, yellow crystals, m. p.  $192^{\circ}$ ; chloride; bromide); 2:6-di-phenyl-4-p-hydroxyphenylpyridine (from the methoxy-compound and concentrated hydrochloric acid at  $160^{\circ}$ ), slender, colourless needles, m. p.  $214-215^{\circ}$  (picrate, yellow crystals, m. p.  $219-220^{\circ}$ ; methiodide, a relatively unstable substance, m. p. about  $190^{\circ}$ , which is converted by sodium picrate into the corresponding picrate, yellow needles, m. p.  $210^{\circ}$ ); 2:6-di-phenyl-4-p-acetoxyphenylpyridine, colourless crystals, m. p.  $110-112^{\circ}$  (picrate, yellow, silky needles, m. p.  $170-171^{\circ}$ ); 4:6-di-phenyl-2-p-anisylpyridine, m. p.  $100-102^{\circ}$  (picrate, m. p.  $210^{\circ}$ ; chloride; bromide; very unstable methiodide); 4:6-di-phenyl-2-p-hydroxyphenylpyridine, m. p.  $189-190^{\circ}$  (chloride, greenish-yellow needles; picrate, yellow crystals, m. p.  $243-244^{\circ}$ ; sodium salt ( $+4H_2O$ ), colourless, silvery leaflets, (anhydrous) lemon-yellow powder; potassium salt; methiodide, coarse, greenish-yellow crystals, m. p.  $208-210^{\circ}$ , and the corresponding picrate, yellow crystals, m. p.  $194^{\circ}$ ); 4:6-di-phenyl-2-p-acetoxyphenylpyridine, colourless needles, m. p.  $113-114^{\circ}$ ; 6-phenyl-2:4-di-p-anisylpyridine, colourless crystals, m. p.  $108-110^{\circ}$  (picrate, lemon-yellow prisms, m. p.  $174-176^{\circ}$ ; bromide, slender, colourless needles; chloride); 6-phenyl-2:4-di-p-hydroxyphenylpyridine (from the preceding compound and concentrated hydrochloric acid at  $160-180^{\circ}$ ), almost colourless needles, m. p.  $222^{\circ}$  (picrate, lemon-yellow prisms, m. p.  $245^{\circ}$ ; bromide, yellow needles; chloride; di-acetyl derivative, m. p.  $140-141^{\circ}$ , and its picrate, small, yellow needles, m. p.  $172^{\circ}$ ; dibenzoyl derivative, colourless needles, m. p.  $147-149^{\circ}$ ; methiodide, unstable, yellow crystals, m. p.  $193-194^{\circ}$  and the corresponding picrate, yellow needles, m. p.  $198-200^{\circ}$  after undergoing alteration at  $134^{\circ}$ ); 4-phenyl-2:6-di-p-anisylpyridine, slender, silky needles, m. p.  $133-134^{\circ}$  (picrate, yellow needles, m. p.  $193-194^{\circ}$ ; chloride, greenish-yellow needles, m. p. (indefinite)  $138-155^{\circ}$ ; bromide, m. p. about  $160^{\circ}$  (indefinite); very unstable methiodide); 4-phenyl-2:6-di-p-hydroxyphenylpyridine (from the

methoxy-compound and hydrochloric acid), almost colourless silky needles, m. p. 228—229°; (*di-potassium salt*, colourless needles; *picrate*, m. p. 256°; *chloride*, yellow needles without definite melting point and the analogous *bromide*; *methiodide*, m. p. 228—229° decomp. and the corresponding *picrate*, orange-yellow crystals, n. p. 250—252°; *di-acetyl derivative*, colourless crystals, m. p. 147—148° and its *picrate*, yellow prisms, m. p. 157—159°; *dibenzoyl compound*, m. p. 206—207°); 2:4:6-*tri-p-anisylpyridine*, colourless, silky needles, m. p. 133° (*picrate*, yellow needles, m. p. 196°; *chloride*, m. p. above 150°; *bromide*, m. p. about 190°, indefinite; unstable *methiodide*, m. p. about 148°); 2:4:6-*tri-p-hydroxyphenylpyridine*, yellowish-white needles, m. p. 282° (*picrate*, m. p. about 293°; *chloride*, yellow needles, m. p. 253°, indefinite; *bromide*, n. p. 334°, indefinite; *methiodide*, yellow, prismatic crystals, m. p. about 228—230°; *tri-acetyl derivative*, colourless prisms, m. p. 58° and its *picrate*, yellow needles, m. p. 182°). H. W.

**Preparation of Aralkyl Esters of 2-Phenylquinoline-4-carboxylic Acid.** SOCIETY OF CHEMICAL INDUSTRY IN BASLE Brit. Pat. 167066).—The aralkyl esters of 2-phenylquinoline-4-carboxylic acid, for example, the benzyl ester, whilst having all the advantages of the alkyl or aryl esters, are, in addition, much better solvents of uric acid. They may be prepared by any of the known methods of esterification. *Benzyl 2-phenylquinoline-4-carboxylate*, prepared, for example, by the action of 1.25 parts of benzyl chloride on 2.5 parts of the sodium salt of the acid suspended in 10 parts of acetone, forms, after suitable purification, citron-yellow crystals, m. p. 77—78°, insoluble in water, but soluble in hydrochloric acid, ether, benzene, or oils. G. F. M.

**Preparation of Disubstituted 2:4-Diketotetrahydro-oxazoles.** SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE ANCT. GILLIARD, P. MONNET & CARTIER (Brit. Pat. 159153).—Disubstituted derivatives of 2:4-diketotetrahydro-oxazole of the general formula  $\text{RR}'\text{C} \begin{smallmatrix} \diagup \text{O}-\text{C}=\text{O} \\ \diagdown \text{CO}-\text{NH} \end{smallmatrix}$  are obtained by the action of chloroformic ester

on the correspondingly disubstituted glycollamide, preferably in the presence of an alkali carbonate and a neutral organic solvent. For example, 450 grams of phenylethylglycollamide dissolved in 10 litres of toluene, after about three hours' boiling with 700 grams of anhydrous potassium carbonate and 300 grams of ethyl chloroformate added gradually during two hours, give a product from which, on treatment with water and sulphuric acid, a nearly theoretical yield of a crystalline mass of 5:5-phenylethyl-2:4-diketotetrahydro-oxazole is obtained. This is purified by distillation in a vacuum (b. p. 176°/3 mm.) and the distillate on cooling yields to a crystalline mass, m. p. 63°. These oxazoles are slightly soluble in hot water and form very soluble, well characterised salts when neutralised with the hydroxides or carbonates of the alkalis and alkaline earths. They have hypnotic and narcotic properties. G. F. M.

**A Comparison of some Isomeric *iso*Cyanines.** FRANCES MARY HAMER (T., 1921, 119, 1432—1444).

**Constitution of the Cyanines.** W. KÖNIG and O. TREICHEL (*J. pr. Chem.*, 1921, 102, 63—84).—The presence of two intact quinoline rings in the cyanines and *isocyanines* was originally formulated by König (A., 1906, i, 207) and largely confirmed by the work of Kaufmann (A., 1911, i, 328; 1912, i, 502). Certain considerations, which are fully outlined in the original, had led König (A., 1912, i, 729) to take into consideration alternative formulæ in which one of the quinoline nuclei has suffered fission of the pyridine ring, and in accordance with which the cyanines and *isocyanines* are to be regarded as condensation products of monoalkylamino-cinnamaldehydes with quinaldinium or lepidinium salts. The authors have therefore endeavoured to prepare synthetically dialkylated substances of the latter type for purposes of spectroscopic and chemical comparison with the cyanines and *isocyanines*. This aim has not been completely achieved owing to the inability to obtain *o*-dimethylaminocinnamaldehyde. It is shown, however, that the absorption curve, in the ultra-violet, of a solution of *p*-dimethylaminocinnamylidenequinaldine methoperchlorate decolorised by hydrochloric acid is widely different from that of a similar solution of *isocyanine*, and that the latter cannot therefore have the "chain" structure. Moreover, since *p*- and *o*-dimethylaminobenzylidenequinaldine methoperchlorates show identical ultra-violet absorption curves (after being decolorised by hydrochloric acid), it follows by analogy that the cyanines also do not contain the open chain. This result is in complete harmony with the observations of Mills and Evans (T., 1920, 117, 1035).

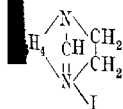
The scope of the investigation has been extended so as to include the examination of a series of condensation products of dimethylaminobenzaldehyde and dimethylaminocinnamaldehyde with  $\alpha$ - and  $\gamma$ -methylcycloammonium salts. The authors are drawn to the conclusions that (1) *o*-dimethylamino-compounds are not true dyes to the same extent as the corresponding para-derivatives, the absorption curves of which have a much more selective character; (2) the substitution of the  $\alpha'$ -phenyl- $\alpha$ -methylpyridine residue for the quinaldine residue has a marked hypsochromic effect; (3) the replacement of a cyclic vinylenic group by a sulphur atom has little influence on the absorption; (4) the streptostatic introduction of the vinylenic group causes a displacement of the maximum of absorption towards the region of longer wave-length without materially altering the form of the curve.

The following individual substances are described: 4-methylquinoline methoperchlorate, m. p. 153°; 6-phenyl-2-methylpyridine methoperchlorate, colourless needles, m. p. 178°; benzothiazole methoperchlorate, m. p. 149°; 1-methylbenzothiazole methoperchlorate, m. p. 126°; *p*-dimethylaminobenzylidene-2-methylquinoline methoperchlorate, red plates, m. p. 274°, and its hydrogen perchlorate, brown needles, m. p. 231°; *p*-dimethylaminobenzylidene-2-methylquinoline ethiodide, prisms, m. p. 249°; *p*-dimethylaminobenzylidene-4-methylquinoline methoperchlorate, green prisms, m. p. 233°; *p*-dimethyl-

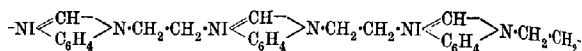
aminobenzylidene-1-methylbenzothiazole methoperchlorate, red needles, m. p. 245°; p-dimethylaminobenzylidene-6-phenyl-2-methylpyridine methoperchlorate, yellowish-red needles, m. p. 189°; o-dimethylaminobenzylidene-2-methylquinoline methoperchlorate, red needles, m. p. 186°; o-dimethylaminobenzylidene-1-methylbenzothiazole methoperchlorate, red leaflets, m. p. 184°; p-dimethylaminocinnamylidene-2-methylquinoline methoperchlorate, lustrous, green crystals, m. p. 243°; p-dimethylaminocinnamylidene-1-methylbenzothiazole methoperchlorate, m. p. 244°; methylisocyanine perchlorate, needles, decomp. above 210°. The dyes are generally prepared by the protracted heating of solutions of molar amounts of the components in methyl or ethyl alcohol in the presence of piperidine as catalyst; in certain cases, acetic anhydride is to be preferred to the latter. H. W.

**Pyro-condensations in the Pyridine Series.** HANS MEYER and ALICE HOFMANN-MEYER (*J. pr. Chem.*, 1921, **102**, 287—294; cf. A., 1917, i, 641; 1918, i, 66).—Pyridine is decomposed at a bright red heat, yielding mainly 2 : 2'-dipyridyl, m. p. 69°, small quantities of 2 : 3' and 2 : 4'-dipyridyl being also formed. The only product from 2-methylpyridine which could be characterised definitely is 6 : 6'-dimethyl 2 : 2'-dipyridyl, but oxidation of the crude product shows that pyro-condensation in this case, in contrast with that of toluene, results essentially in the union of the nuclei, which is in accordance with the known greater stability of the methyl group in the 2'-position attached to the pyridine nucleus. 2 : 6-Dimethylpyridine gives a tetramethyldipyridyl, colourless needles grouped in rosettes, m. p. 55°, of unknown constitution. 2 : 4 : 6-Trimethylpyridine yields a hexamethyldipyridyl (monohydrate, colourless solid, m. p. 66—69°) and an oil which resembles quinoline in odour, but from which a uniform material could not be isolated. H. W.

**1-Vinylbenziminazole.** JAKOB MEISENHEIMER and BRUNO WIEGER (*J. pr. Chem.*, 1921, **102**, 45—62).—A record of further attempts to obtain stereoisomeric compounds containing tervalent nitrogen (cf. A., 1920, i, 761). The introduction of a side chain of two or three carbon atoms to one of the nitrogen atoms of tetrahydroquinoxaline proved exceptionally difficult, since only resinous products, from which a homogeneous material could not be isolated, resulted from the application of ethylene bromide, ethylene chlorobromide, glycol chlorohydrin, propylene chlorobromide, or  $\beta$ -chloropropaldehyde acetal. It was also found impossible to protect one of the imino-groups by acetylation or benzoylation, since only the di-substituted products could be prepared. Benziminazole, on the other hand, was successfully transformed into 1- $\beta$ -iodoethylbenziminazole,  $N \begin{smallmatrix} \text{CH} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{smallmatrix} N \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{I}$  which, however, did not



suffer intramolecular alkylation to a compound of the annexed type when treated with alcoholic potassium hydroxide, but lost hydrogen iodide with formation of 1-vinylbenziminazole. The iodide, when heated by itself, undergoes intermolecular alkylation, yielding a polymeride of the desired substance of the type :



Tetrahydroquinoxaline is converted by benzoyl chloride in acetone solution into *dibenzoyltetrahydroquinoxaline*, m. p. 201.5°.

Benziminazole is very readily prepared by the action of formic acid on *o*-phenylenediamine if the initial materials are pure; it gives a *picrate*, slender, golden-yellow needles, m. p. 223°. It can be converted into 1-β-hydroxyethylbenziminazole by treatment with an excess of glycol chlorohydrin at the laboratory temperature in the presence of aqueous alkali, by heating the components in toluene solution or, less advantageously, by heating without a solvent. The most satisfactory process, however, consists in the union of benziminazole with ethylene oxide in the presence of a little water, the formation of by-products being almost entirely avoided if the temperature is kept sufficiently low. The crude material is purified by way of the *picrate*, pale yellow needles, m. p. 204°. Pure N-β-hydroxyethylbenziminazole has m. p. 107–108° (*hydrochloride*, coarse, colourless needles, m. p. 183–184°, *platinichloride*, orange-red prisms, m. p. 189–190°). It is converted by boiling fuming hydriodic acid (*d* 1.99) in the presence of red phosphorus into 1-β-iodoethylbenziminazole *hydriodide*, m. p. 174–175° after softening at 170°. The corresponding free base is a pale yellow, viscous liquid which, on account of its instability, could not be purified completely; it gives a *picrate*, m. p. 196–197° (decomp.). The hydriodide is converted by boiling methyl alcoholic sodium methoxide solution into 1-vinylbenziminazole, b. p. 144–146°/12 mm., which rapidly darkens when exposed to light and air, but can be preserved in a vacuum for a considerable period without change. It is converted by concentrated hydriodic acid into 1-β-iodoethylbenziminazole and by boiling dilute hydrochloric acid into the corresponding ethanol. It gives a *picrate*, m. p. 194–195° (decomp.), and a *platinichloride*, decomp. 240–245°.

1-β-Iodoethylbenziminazole becomes converted at 100° into the colourless, amorphous polymeric *iodide*, m. p. above 360°; the corresponding *picrate* does not melt below 360°. Attempts to isolate a homogeneous free base were unsuccessful. H. W.

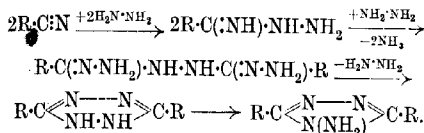
### **spiro-Pyrimidines. II. cycloHexane-1:5-spiropyrimidines.**

ARTHUR W. DOX and LESTER YODER (*J. Amer. Chem. Soc.*, 1921, 43, 1366–1370; cf. this vol., i, 360).—α-ε-Dibromopentane was prepared by a slight modification of von Braun's method (cf. A., 1904, i, 841), using phosphorus tribromide and benzoylpiperidine, and subsequently removing the benzonitrile from the dibromopentane by shaking the mixture with cold concentrated sulphuric acid. α-ε-Dibromopentane condenses with ethyl malonate (*loc. cit.*) to give *ethyl cyclohexane-1:1-dicarboxylate*, b. p. 105–106°/5 mm., the corresponding *amide* having m. p. 237°. The ester condenses with carbamide to give *cyclohexane-1:5-spiro-2:4:6-triketohexahydropyrimidine*,  $\text{CH}_2 \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \text{C} \begin{array}{c} \text{CO} \cdot \text{NH} \\ \diagup \quad \diagdown \\ \text{CO} \cdot \text{NH} \end{array} \text{CO}$ , m. p. 281°.

and with guanidine giving cyclohexane-1 : 5-spiro-2-imino-4 : 6-diketohexahydropyrimidine.

W. G.

**Action of Anhydrous Hydrazine on Nitriles.** ERNST MÜLLER and LEONHARD HERRDEGEN (*J. pr. Chem.*, 1921, **102**, 113—155).—The action of hydrazine on an extensive series of aliphatic and aromatic nitriles has been investigated. In the  $\alpha$ -mer group, the ability to react declines rapidly with increasing molecular weight of the nitrile. The course of the change may be represented by the general scheme :



3 : 6-Dimethyldihydro-1 : 2 : 4 : 5-tetrazine and 3 : 6-dimethyl-*s*-triazine are prepared by the method of Curtius, Darapsky, and Müller (A., 1916, i, 84); the absorption spectrum of the latter has been investigated. It is hydrolysed by boiling dilute acids in a complicated manner, yielding nitrogen, hydrazine, and acetic acid; the formation of acetaldehyde or ammonia could not be established. Propionitrile and hydrazine slowly yield 3 : 6-diethyldihydro-1 : 2 : 4 : 5-tetrazine, which was not isolated in the homogeneous condition, and 4-amino-2 : 5-diethyl-1 : 3 : 4-triazole, colourless, silky needles, m. p. 60°. The former is oxidised readily to 3 : 6-diethyltetrazine, which could only be obtained as a viscous, red liquid; it is hydrolysed by acid in the same manner as the dimethyl compound. Butyronitrile and hydrazine give the corresponding tetrazine in too small quantity to permit further investigation, whilst isovaleronitrile does not react perceptibly with hydrazine, even after protracted heating.

3 : 6-Diphenyldihydro-1 : 2 : 4 : 5-tetrazine, m. p. 191°, is produced from benzonitrile and anhydrous hydrazine readily at 100°, slowly at the atmospheric temperature, and is transformed by nitrous acid into 3 : 6-diphenyltetrazine, m. p. 195°; the latter is hydrolysed by acid with the formation of nitrogen, hydrazine, benzaldehyde, benzoic acid, and 2 : 5-diphenyl-1 : 3 : 4-oxadiazole, m. p. 137—138°, but the relative amounts of these products indicate considerable complexity in the change.

The slow formation of a tetrazine is observed when a mixture of benzyl cyanide and hydrazine is boiled for several days, but the product could not be isolated in substance, 1-amino-2 : 5-dibenzyl-1 : 3 : 4-triazole, m. p. 166·5°, being obtained in its place. The components do not react with one another at the laboratory temperature.

*p*-Toluenitrile is slowly transformed into di-*p*-tolyldihydro-1 : 2 : 4 : 5-tetrazine, pale yellow needles, m. p. 223°, which is converted by nitrous acid into di-*p*-tolyltetrazine, m. p. 232°. *m*-Toluenitrile readily yields 3 : 6-di-*m*-tolyldihydro-1 : 2 : 4 : 5-tetrazine, small, golden-yellow needles, m. p. 194—195°, after darkening above 159°, which is hydrolysed by concentrated hydrochloric acid initially to hydrazine chloride and

*ee*\*



2:5-di-*m*-tolyl-1:3:4-oxadiazole, m. p. 72–73°, after softening at 67°, and ultimately to hydrazine and *m*-toluic acid. It is readily oxidised to 3:6-di-*m*-tolyl-1:2:4:5-tetrazine, red needles, m. p. 150–152°, which is converted by boiling dilute acid into nitrogen, hydrazine, and *m*-toluic acid, *m*-tolualdehyde appearing not to be formed. Protracted ebullition of a mixture of *m*-toluonitrile and anhydrous hydrazine leads to the production of 1-amino-2:5-di-*m*-tolyl-1:3:4-triazole, colourless leaflets, m. p. 176–177° (decomp.). *o*-Toluonitrile, on the other hand, does not appear to react with anhydrous hydrazine.

$\beta$ -Naphthonitrile reacts in the same manner as *p*-toluonitrile, yielding 3:6-di- $\beta$ -naphthyl-dihydrotetrazine, slender, yellow needles, m. p. 239–240°, which is readily transformed into 3:6-di- $\beta$ -naphthyl-tetrazine, red crystals, m. p. 249°; the dihydro-compound is converted by boiling acids, to a small extent only, into hydrazine and  $\beta$ -naphthoic acid, the main hydrolysis occurring in the direction of hydrazine and 2:5-di- $\beta$ -naphthyl-1:3:4-oxadiazole, m. p. 210–211°.

When absolute hydrocyanic acid and anhydrous hydrazine are mixed very cautiously at the temperature of a freezing mixture, the very unstable *diammonium cyanide*,  $N_2H_5 \cdot CN$ , is obtained as a colourless, crystalline mass, m. p. 17° (cf. Franzen and Lucking, A., 1911, ii, 285). If it is melted and subsequently heated to 55°, a yellow liquid is produced which solidifies in a vacuum to a yellow, crystalline *substance*, probably dimethinehydrazodihydrazone,  $NH_2 \cdot N \cdot CH \cdot NH \cdot NH \cdot CH \cdot N \cdot NH_2$ , formed in accordance with the scheme  $CH(NH) \cdot NH \cdot NH_2 \xrightarrow[-NH_2]{+N_2H_5} CH(N \cdot NH_2) \cdot NH \cdot NH_2 +$

$CH(NH) \cdot NH \cdot NH_2 \xrightarrow{-NH_2} NH_2 \cdot N \cdot CH \cdot NH \cdot NH \cdot CH \cdot N \cdot NH_2$ . The

main evidence of its constitution rests on its conversion into a *benzylidene* derivative, m. p. 99°, after softening at 94°, of approximately the expected composition. When the dimethine compound is treated with sodium nitrite and acetic acid, it is converted into 1:2:4:5-tetrazine, which, on reduction with zinc dust in ethereal solution, passes into dihydrotetrazine, m. p. 117–119°, whereas Curtius, Darapsky, and Müller (*loc. cit.*) give m. p. 125–126°. 1-Amino-1:3:4-triazole, m. p. 83°, is formed when *diammonium cyanide* is heated at 120° until ammonia is no longer evolved. H. W.

**Reduction of Aromatic Azo-compounds and Nitro-compounds.** TOM SIDNEY MOORE (Brit. Pat. 165838).—Aromatic azo-compounds and nitro-compounds are reduced to amines by the action of a relatively large quantity of iron filings or borings in presence of water and a relatively small quantity of sulphur dioxide, considerably less than would be required to generate a quantity of ferrous hyposulphite sufficient to effect the reduction. For example, *p*-nitrophenol (1 part) is reduced to *p*-aminophenol by boiling with 4 parts of iron and 5 parts of water, 0.2 part of sulphurous acid in aqueous solution being gradually added during one hour. When reduction is complete, sodium carbonate and sulphite are added, and the boiling solution is separated from the

iron sludge by filtration. White crystals of the amine are deposited from the filtrate, and the total yield amounts to about 80% of the theoretical. The probable course of the reaction is not indicated. In a similar way, *p*-aminophenol and sulphanilic acid are obtained by the reduction of sodium *p*-hydroxyazobenzene-*p*-sulphonate, 2:4-diaminophenol from dinitrophenol, the phenylenediamines from the nitroanilines, etc.

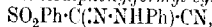
G. F. M.

**Isonitriles. I. Compound of *p*-isoNitriloazobenzene [*p*-Carbylaminoazobenzene].** M. PASSERINI (*Gazzetta*, 1921, 51, ii, 126—129).—When *p*-carbylaminoazobenzene is treated, in acetone solution, with acetic acid and hydrogen peroxide (this vol. i, 197), confinement of the oxidising action solely to the isonitrilo-group takes place to only a very small extent; the reaction yields, indeed, a very small proportion of 4:4'-carbaminoazobenzene, which is evidently formed by the action of the water, introduced with the hydrogen peroxide, on the azobenzene *p*-carbinide formed by oxidation of the isonitrile. The principal product of the reaction consists of the acetyl derivative of hydroxyisobutryl-*p*-aminoazobenzene,  $\text{NPh}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CMe}_2\cdot\text{OAc}$ , m. p. 147—148°; the formation of this compound, which yields hydroxyisobutryl-*p*-aminoazobenzene on hydrolysis, is probably preceded by that of a labile additive compound of acetic acid and acetone,  $\text{OH}\cdot\text{CMe}_2\cdot\text{OAc}$ , this then reacting with the isonitrile; that the acetone does not act first as hydrate and the acetic acid subsequently is shown by the fact that the reaction takes place in a medium as nearly dry as possible and by the difficulty experienced in acetylating the hydrolysed product.

The compound, m. p. 222—223°, obtained from benzaldehyde and *p*-carbylaminoazobenzene, and previously regarded as an additive compound (*loc. cit.*), is probably of similar structure to that given by acetic acid, its formation being due to the presence of benzoic acid in the aldehyde used; an increased yield is, indeed, obtained when benzoic acid is employed in place of benzaldehyde.

T. H. P.

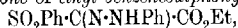
**The Action of Diazonium Salts on Benzene- and *p*-Toluene-sulphonyl Derivatives of Acetic Acid, Ethyl Acetate, Acetonitrile, and Acetamide.** J. TRÖGER and A. BERNDT (*J. pr. Chem.*, 1921, 102, 1—35).—The addition of a solution of benzenediazonium chloride to benzenesulphonylacetonitrile dissolved in the equivalent quantity of aqueous sodium hydroxide or to an alcoholic solution of the nitrile in the presence of concentrated aqueous sodium acetate solution leads to the formation of benzenesulphonylbenzenesulphonylacetonitrile,  $\text{SO}_2\text{Ph}\cdot\text{CH}(\text{N}_2\text{Ph})\cdot\text{CN}$ , or the benzylhydrazone of benzenesulphonylformyl cyanide,



golden-yellow, prismatic needles, m. p. 160° [the sodium salt, yellow, quadratic leaflets ( $\frac{1}{2}\text{H}_2\text{O}$ ), potassium, lead, and silver salts of which were analysed]. Similar methods lead to the production of the following substances which, for the sake of brevity, are cited as azo-compounds, although the possibility of their hydrazone nature

is by no means excluded: *benzenesulphonyl-m-tolueneazoacetone nitrile*, coarse, dark-red needles, m. p. 153—154°, and its sodium (+2H<sub>2</sub>O), *potassium*, *lead*, and *silver* salts; *benzenesulphonyl-o-tolueneazoacetone nitrile*, yellow or brownish-red crystals, m. p. 154°, and its sodium and *potassium* salts, which can be prepared in the absence of water; *benzenesulphonyl-p-tolueneazoacetone nitrile*, red, prismatic needles, m. p. 172°, and its sodium (+2H<sub>2</sub>O), *potassium*, *lead*, and *silver* salts; *benzenesulphonyl-o-methoxybenzeneazoacetone nitrile*, small, rust-brown needles, m. p. 165°, and its sodium, *potassium*, *lead*, and *silver* salts; *benzenesulphonyl-p-methoxybenzeneazoacetone nitrile*, small, pale yellow needles, m. p. 159°, and its sodium and *potassium* salts; *benzenesulphonyl-as-m-xylyleneazoacetone nitrile*, brownish-red leaflets, m. p. 164—165°, and its sodium, *potassium*, *lead*, and *silver* salts; *benzenesulphonyl-p-ethoxybenzeneazoacetone nitrile*, ruby-red needles, m. p. 173°, and its sodium, *potassium* (+2H<sub>2</sub>O), *lead*, and *silver* salts; *p-toluenesulphonylbenzeneazoacetone nitrile*, golden-yellow, lustrous needles, m. p. 144°, the alkali salts of which could not be isolated, even in the absence of water; *p-toluenesulphonyl-o-tolueneazoacetone nitrile*, small, greenish-yellow, prismatic needles, m. p. 152°, the alkali salts of which could not be isolated; *p-toluenesulphonyl-m-tolueneazoacetone nitrile*, yellowish-brown prisms, m. p. 135°, and its sodium salt (+2H<sub>2</sub>O); *p-toluenesulphonyl-p-tolueneazoacetone nitrile*, yellow, prismatic needles, m. p. 154°, and its sodium salt (+2H<sub>2</sub>O); *p-toluenesulphonyl-o-methoxybenzeneazoacetone nitrile*, yellow, prismatic needles, m. p. 176°, and its sodium salt (+2H<sub>2</sub>O); *p-toluenesulphonyl-p-methoxybenzeneazoacetone nitrile*, egg-yellow crystals, m. p. 145°, and its oily sodium and *potassium* (+H<sub>2</sub>O) salts; *p-toluenesulphonyl-p-ethoxybenzeneazoacetone nitrile*, prisms, m. p. 143°; *p-toluenesulphonyl-as-m-xylyleneazoacetone nitrile*, pale yellow crystals, m. p. 151°.

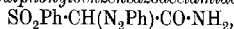
All the nitriles described above are unusually stable towards hydrolysing agents, and it was not found possible to secure conditions under which the cyano- was converted into the carboxyl group without profound change in the remainder of the molecule. In the hope of securing a path to the acids, the action of diazonium salts of the benzene- and *p*-toluene-sulphonyl derivatives of ethyl acetate was therefore investigated. In this case, the sodium acetate method is not applicable, and the following compounds were prepared by the neutralisation of the mineral acid liberated during coupling by cautious addition of sodium hydroxide solution: *ethyl benzenesulphonylbenzeneazoacetate*, SO<sub>2</sub>Ph·CH(N<sub>2</sub>Ph)·CO<sub>2</sub>Et, or the phenylhydrazone of *ethyl benzenesulphonylglucosylate*,



yellow prisms, m. p. 140°, and its sodium salt, which can be prepared only in the absence of water; *ethyl benzenesulphonyl-p-tolueneazoacetate*, dark yellow, prismatic needles, m. p. 128°; *ethyl benzenesulphonyl-m-tolueneazoacetate*, small, pale yellow needles, m. p. 102°; *ethyl benzenesulphonyl-o-tolueneazoacetate*, reddish-yellow prisms, m. p. 120°; *ethyl benzenesulphonyl-p-methoxybenzeneazoacetate*, reddish-brown prisms, m. p. 147°; *ethyl benzenesulphonyl-o-methoxybenzeneazoacetate*, greenish-yellow, silky leaflets,

m. p. 143°; *ethyl benzenesulphonyl-p-ethoxybenzeneazooacetate*, small prisms, m. p. 134°; *ethyl benzenesulphonyl-as-m-xyleneazooacetate*, reddish-yellow leaflets, m. p. 146°, and its sodium salt; *ethyl p-toluenesulphonylbenzeneazooacetate*, orange-yellow needles, m. p. 134°; *ethyl p-toluenesulphonyl-p-tolueneazooacetate*, dark orange crystals, m. p. 129°; *ethyl p-toluenesulphonyl-m-tolueneazooacetate*, pale brown prisms, m. p. 155°; *ethyl p-toluenesulphonyl-o-tolueneazooacetate*, slender, yellow prisms, m. p. 132°, and its sodium salt; *ethyl p-toluenesulphonyl-o-methoxybenzeneazooacetate*, dark green, silky needles, m. p. 157°; *ethyl p-toluenesulphonyl-p-methoxybenzeneazooacetate*, greenish-brown prisms, m. p. 144°; *ethyl p-toluenesulphonyl-p-ethoxybenzeneazooacetate*, reddish-brown crystals, m. p. 140°; *ethyl p-toluenesulphonyl-as-m-xyleneazooacetate*, tile-red prisms, m. p. 159°, and its sodium salt.

Attempts to isolate uniform products by the hydrolysis of the esters just described were not successful, and the preparation of the acetamide derivatives was therefore undertaken. In this instance, the use of sodium acetate and sodium hydroxide respectively leads to the formation of different substances of the same percentage composition; it is considered, with some reserve, that the products obtained by the former method are analogous with those from the nitrile or ester. The following individuals are described: *benzenesulphonylbenzeneazooacetamide*,



or the *phenylhydrazone of benzenesulphonyl-glyoxylamide*,

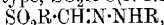


yellowish-brown crystals, m. p. 158°, and its sodium salt; *benzenesulphonyl-m-tolueneazooacetamide*, reddish-brown, pointed needles, m. p. 152°, and its sodium salt; *benzenesulphonyl-o-tolueneazooacetamide*, slender, pale-yellow needles, m. p. 181°; *benzenesulphonyl-p-tolueneazooacetamide*, tile-red, prismatic needles, m. p. 195°; *benzenesulphonyl-p-methoxybenzeneazooacetamide*, reddish-yellow, quadratic crystals, m. p. 151°; *benzenesulphonyl-o-methoxybenzeneazooacetamide*, golden-yellow needles, m. p. 162°; *benzenesulphonyl-p-ethoxybenzeneazooacetamide*, pale yellow, quadratic crystals, m. p. 174°; *benzenesulphonyl-as-m-xyleneazooacetamide*, golden-yellow, prismatic needles, m. p. 204°; *p-toluenesulphonylbenzeneazooacetamide*, reddish-brown, lustrous prisms, m. p. 134°; *p-toluenesulphonyl-p-tolueneazooacetamide*, brownish-red crystals, m. p. 170°; *p-toluenesulphonyl-m-tolueneazooacetamide*, yellowish-brown crystals, m. p. 158°; *p-toluenesulphonyl-o-tolueneazooacetamide*, yellow needles, m. p. 169°; *p-toluenesulphonyl-p-methoxybenzeneazooacetamide*, ruby-red needles, m. p. 151°, and its sodium salt; *p-toluenesulphonyl-o-methoxybenzeneazooacetamide*, blood-red crystals, m. p. 162°; *p-toluenesulphonyl-p-ethoxybenzeneazooacetamide*, blood-red crystals, m. p. 164°; *p-toluenesulphonyl-as-m-xyleneazooacetamide*, brownish-yellow prisms, m. p. 200°. The hydrolysis of these amides has not been studied completely.

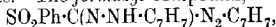
The following products are obtained by the use of sodium hydroxide for neutralisation of the acid liberated during coupling (cf. above); their constitution has not been elucidated: *compound*,

$C_{15}H_{15}O_3N_3S$  (from benzenesulphonylacetic acid and *o*-toluene-diazonium chloride), red, prismatic needles, m. p.  $190^\circ$ ; *compound*,  $C_{15}H_{15}O_3N_3S$  (from *p*-toluenesulphonylacetic acid and benzenesulphonyl chloride), brownish-red, prismatic leaflets, m. p.  $160^\circ$ ; *compound*,  $C_{16}H_{17}O_3N_3S$  (from *p*-toluenesulphonylacetic acid and *o*-toluenediazonium chloride), tile-red needles, m. p.  $178^\circ$ ; *compound*,  $C_{16}H_{17}O_3N_3S$  (from *p*-toluenesulphonylacetic acid and diazotised *o*-anisidine), dark red, iridescent needles, m. p.  $200^\circ$ .

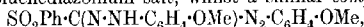
The action of solutions of diazonium salts on the free acids follows a complex course which depends, in part, at any rate, on the use of sodium hydroxide or sodium acetate for the removal of liberated mineral acid. With the former reagent, it is established that elimination of the  $R\cdot SO_2\cdot$  group does not take place and that compounds of the type,  $SO_2R\cdot C(N\cdot NHR)\cdot CO_2H$ , or



are formed with difficulty or not at all. Formazyl compounds, or mixtures of the latter and hydrazones, are produced. In a large number of instances exceptional experimental difficulties are encountered owing to the absence of a suitable solvent or the impossibility of separating the complex products into their individual components. The *formazyl* compound,



dark red leaflets, m. p.  $161^\circ$ , could, however, be isolated from benzenesulphonylacetic acid and two or more molecular proportions of *o*-toluenediazonium salt, whilst a similar *compound*,



slender, greenish-red needles, m. p.  $197^\circ$ , is prepared by the use of diazotised *o*-anisidine. In the presence of sodium acetate, benzenediazonium chloride yields with benzene- or *p*-toluenesulphonylacetic acid a *compound*, brown needles, m. p.  $135^\circ$ , which is free from sulphur; its constitution has not been elucidated. In a similar manner, benzenesulphonylacetic acid and *o*-toluenediazonium chloride give a sulphur-free *product*, slender, brown needles, m. p.  $146^\circ$ .

H. W.

**Hydrazones and Azines. II. Condensation Products of Aromatic Ketohydrazones with Orthoquinones.** OTTO GERHARDT (*Monatsh.*, 1921, 42, 63–72; cf. A., 1920, i, 766).—It has been shown previously that little connexion between colour and constitution is exhibited by ketazines, but the formation of intensely coloured products is to be expected by the union of the azomethylene group,  $C=N_2$ , with quinonoid nuclei. The behaviour of aromatic ketazines towards quinones has therefore been investigated. With *p*-benzoquinone and  $\alpha$ -naphthaquinone, the main result consists in the oxidation of the ketazine with formation of indefinite products. With more complex orthoquinones, on the other hand, the oxidising action is but little in evidence, and, of the possible reactions,  $CR'_2\cdot N\cdot NH_2 + O\cdot R\cdot O \rightarrow CR'_2\cdot N\cdot N\cdot R\cdot O$  and  $2CR'_2\cdot N\cdot NH_2 + O\cdot R\cdot O \rightarrow CR'_2\cdot N\cdot N\cdot R\cdot N\cdot N\cdot CR'_2$ , it has been found possible to realise the first, but not the second. The condensation products, for which the term "quinaketazines" is

proposed, are generally prepared in good yield by boiling a solution of molar quantities of the components in a dry hydrocarbon of the benzene series. The following individuals are described.

*Phenanthrenequinobenzophenoneketazine*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{C:N}_2\text{:CPh}_2$ , dark red crystals, m. p. 158—159°; *phenanthrenequinofluorenoneketazine*, brownish-violet crystals, m. p. 215—216°; *acenaphthenequinobenzophenoneketazine*, yellow crystals, m. p. 185—186°; *isatobenzophenoneketazine*,  $\text{NH} \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{C:N}_2\text{:CPh}_2$ , canary-yellow crystals, m. p. 214—215°; *acenaphthenequinofluorenoneketazine*, brownish-yellow crystals, m. p. 193.5—195°; *isatofluorenoneketazine*, slender, cinnabar-red crystals, m. p. 185—186°; *thionaphthenequinobenzophenoneketazine*,  $\text{S} \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{C:N}_2\text{:CPh}_2$ , lustrous, cinnabar-red crystals, m. p. 107—108.5°; *thionaphthenequinofluorenoneketazine*, dark red needles, m. p. 221—223°; *camphorquinobenzophenoneketazine* (annexed formula), almost colourless, crystalline powder, m. p. 106.5—108°; *camphorquinofluorenoneketazine*, a colourless, crystalline powder, m. p. 156—157°. H. W.

**Preparation of Nitro-derivatives of  $\beta$ -Azides of the Anthraquinone Series.** FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.P. 337734; from *Chem. Zentr.*, 1921, iv, 262).— $\beta$ -Azides of the anthraquinone series are treated with strong nitric acid or nitric and sulphuric acids. The nitro-group enters the  $\alpha$ -position next to the azide group. 1-Nitro-2-azidoanthraquinone, prepared by the action of fuming nitric acid on 2-azidoanthraquinone, forms yellowish-green crystals becoming light orange-red on exposure to light and air, m. p. 210° (decomp.). On heating an aqueous suspension with sodium sulphide, the colour becomes green and then violet, and by further heating 1 : 2-diaminoanthraquinone crystallises out with evolution of nitrogen. By addition of 2 : 6-diazidoanthraquinone to cold fuming nitric acid or a solution of potassium nitrate in strong sulphuric acid with cooling, 1 : 5-dinitro-2 : 6-diazidoanthraquinone separates in yellow crystals which, after recrystallisation from nitrobenzene, form light yellow needles, m. p. 200°; at 202°, sudden decomposition takes place with separation of carbon. Reduction with sodium sulphide gives 1 : 2 : 5 : 6-tetraaminoanthraquinone. G. W. R.

**The Hydrazide and Azide of Benzylsulphonic Acid.** THEODOR CURTIUS and FRIEDRICH WILHELM HAAS (*J. pr. Chem.*, 1921, 102, 85—112).—The substances named in the title have been prepared as examples of this class of compounds in which the sulphonhydrazide and sulphonazide groups are attached to an aromatic radicle instead of directly to an aromatic nucleus. In general, they show a close resemblance to the corresponding compounds of benzenesulphonic acid (cf. Curtius and Rissom, *Zeitsch. angew. Chem.*, 1913, 26, [iii], 134).

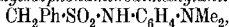
*Benzylsulphonhydrazide*,  $\text{CH}_2\text{Ph}\cdot\text{SO}_2\cdot\text{NH}\cdot\text{NH}_2$ , colourless crystals, m. p. 131—132° (decomp.), is obtained by the action of hydrazine hydrate on benzylsulphonyl chloride in cold, absolute alcoholic solution. It decomposes in boiling aqueous solution into nitrogen, hydrogen, and benzyldisulphonic acid, but attempts to isolate di-imide (which is presumably formed intermediately during the reaction) in the form of its silver salt were unsuccessful. When silver nitrate is added to solutions from which much gas has been evolved, a precipitate is formed which blackens rapidly; when, however, the reagent is added to a slightly decomposed solution, the salt,  $(\text{CH}_2\text{Ph}\cdot\text{SO}_2\cdot\text{NH}\cdot\text{NH}_2)_2\cdot\text{AgNO}_3$ , is precipitated in colourless leaflets. Benzylsulphonhydrazide gives a *hydrochloride*, small, colourless needles, m. p. 148° (decomp.), and a *benzylidene derivative*,  $\text{CH}_2\text{Ph}\cdot\text{SO}_2\cdot\text{NH}\cdot\text{N}:\text{CHPh}$ , colourless needles, m. p. 139.5° (decomp.). When subjected to protracted heating in almost absolute alcoholic solution it gives *diammonium benzyldisulphonate*,  $\text{CH}_2\text{Ph}\cdot\text{SO}_3\cdot\text{N}_3\text{H}_3$ , colourless needles, decomp. about 150°, benzyldisulphonic acid, nitrogen, and hydrogen.

*Benzylsulphonazide*,  $\text{CH}_2\text{Ph}\cdot\text{SO}_2\cdot\text{N}_3$ , colourless, slender needles, m. p. 54°, is prepared by the action of nitrous acid on the corresponding hydrazide or from benzylsulphonyl chloride and sodium azide in alcoholic solution. When heated with hydrocarbons, it behaves in a similar manner to benzenesulphonazide, evolving two-thirds of its nitrogen and leaving a residue,  $\text{CH}_2\text{Ph}\cdot\text{SO}_2\cdot\text{N}<$ , which unites with the solvent. With boiling toluene, reaction is very slow, but with *p*-xylene, *benzylsulphon-p-xylidide*,  $\text{CH}_2\text{Ph}\cdot\text{SO}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}_2$ , pale yellow needles, m. p. 124°; the latter is hydrolysed by concentrated hydrochloric acid to *p*-xylidine, toluene, and sulphur dioxide. The occurrence of the latter is surprising, since the formation of sulphuric acid would be expected; the presence of benzyl chloride or benzyl alcohol in the toluene, which would account for the reaction, could not be demonstrated. Similarly, benzyldisulphonazide and naphthalene give *benzylsulphon- $\alpha$ -naphthalide*, yellow needles, m. p. 146°, which is identical in all respects with the synthetic product (*benzylsulphon- $\beta$ -naphthalide* crystallises in needles, m. p. 148.5°); it is hydrolysed by hydrochloric acid to  $\alpha$ -naphthylamine hydrochloride, sulphur dioxide, and resinous matter, which doubtless originates from benzyl alcohol.

Two reactions occur concurrently when benzyldisulphonazide is heated with aniline. The first of these leads to the formation of hydrazoic acid and *benzylsulphonanilide*, colourless needles, m. p. 102°, in accordance with the equation  $\text{CH}_2\text{Ph}\cdot\text{SO}_2\cdot\text{N}_3 + \text{NH}_2\text{Ph} = \text{CH}_2\text{Ph}\cdot\text{SO}_2\cdot\text{NHPh} + \text{N}_3\text{H}$ , whilst the second gives rise to the residue,  $\text{CH}_2\text{Ph}\cdot\text{SO}_2\cdot\text{N}$ , which combines with two atoms of hydrogen, yielding benzyldisulphonamide. Since the hydrogen atoms are derived from aniline, it was expected that benzidine would be formed as anti-substance, but no trace of this substance could be detected. On the other hand, considerable quantities of *pp'*-diaminotriphenylmethane are formed which originate in the following manner. In addition to the usual action which leads to the normal anilide, benzyldisulphonazide decomposes in accordance with the scheme

$\text{CH}_2\text{Ph}\cdot\text{SO}_2\cdot\text{N}_3=\text{Ph}\cdot\text{CH}\cdot+\text{SO}_2+\text{N}_3\text{H}$ ; the residue,  $\text{Ph}\cdot\text{CH}\cdot$ , unites subsequently with two of the aniline residues liberated by the formation of the sulphonamide according to the equation  $\text{CH}_2\text{Ph}\cdot\text{SO}_2\cdot\text{N}_3+2\text{Ph}\cdot\text{NH}_2=\text{CH}_2\text{Ph}\cdot\text{SO}_2\cdot\text{NH}_2+\text{N}_3+2\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot$ , thus giving *pp'*-diaminotriphenylmethane. It is noticeable that the reaction  $\text{CH}_2\text{Ph}\cdot\text{SO}_2\cdot\text{N}_3+\text{Ph}\cdot\text{NH}_2=\text{CH}_2\text{Ph}\cdot\text{SO}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2+\text{N}_2$  does not appear to take place, although this is the main change suffered by benzenesulphonazide.

The main product of the action of benzylsulphonazide on dimethylaniline is benzylsulphonaminodimethylaniline,



colourless crystals, m. p.  $127^\circ$ ; the definite melting point of the crude product indicates that it is homogeneous and, probably, the para-derivative. As by-products, sulphur dioxide, hydrazoic acid, ammonium hydrazoate, and *pp'*-tetramethyldiaminotriphenylmethane are obtained.

H. W.

**A New Method for the Preparation of  $\alpha$ -Acylphenylhydrazones.** WALLACE FRANK SHORT (T., 1921, 119, 1445—1448).

**Decomposition of Aldehydo-phenylhydrazones.** R. CIUSA (*Gazzetta*, 1921, 51, ii, 125).—The catalytic reduction of aldehydo-phenylhydrazones into aniline and the nitrile corresponding with the nitrile observed by Mailhe (this vol., i, 463) occurs also when such phenylhydrazones are heated with certain metallic chlorides (Arbuzov, A., 1913, i, 347), and the present author gave the formation of benzonitrile and aniline when benzaldehydephenylhydrazone is heated with zinc chloride as an illustration of the analogy existing between the oximes and hydrazones (A., 1908, i, 833). T. H. P.

**The Albumin of the White of Hens' Eggs.** S. P. L. SÖRENSEN (*Bull. Soc. chim.*, 1921, [iv], 29, 593—624).—A lecture delivered before the Chemical Society of France on May 13, 1921. A. A. E.

**The Preparation and Recrystallisation of Oxyhæmoglobin.**

HAROLD WARD DUDLEY and CHARLES LOVATT EVANS (*Biochem. J.*, 1921, 15, 487—488).—Defibrinated horse blood is centrifuged and the corpuscles are washed with normal saline solution until the washings give no turbidity on boiling. The corpuscles are then dialysed in collodion tubes under pressure against tap and distilled water. The laked corpuscles are centrifuged and the hæmoglobin solution is re-oxygenated. The less soluble oxyhæmoglobin crystallises out suddenly after about twenty minutes. For recrystallisation, the crystals are suspended in 2—3 volumes of water and warmed to  $37^\circ$  in a vacuum, when a clear hæmoglobin solution results. On again passing oxygen into the cooled solution, the oxyhæmoglobin crystallises once more.

G. B.

**Osmosis and Swelling of Gelatin.** C. R. SMITH (*J. Amer. Chem. Soc.*, 1921, 43, 1350—1366).—Gelatin, free from ash, was used in the experimental work. It was prepared by extracting finely-powdered gelatin in a filter with 10% sodium chloride solution containing about 5 c.c. of concentrated hydrochloric acid per litre until the washings showed no reaction for calcium. The



washing was then continued with 1% sodium chloride solution without acid, the concentration of the solution being diminished as rapidly as control of the swelling would permit. Final washing was effected with distilled water, until the washings were free from chlorides, when 90% alcohol was poured through the mass, which was finally dried in an oven.

The osmotic pressure of this gelatin in the presence of water is proportional to concentration and gives a molecular weight of 96,000, assuming the applicability of the gas laws. Gelatin sols in a collodion membrane immersed in isohydric solutions of univalent acids, or multivalent acids ionising as univalent acids, produce the same osmotic pressure. Similarly, in univalent bases the same osmotic pressure is produced at the same hydroxyl-ion concentration. Minimum osmotic pressure is produced at the isoelectric point where it is not combined with acids or bases and with increasing hydrogen- or hydroxyl-ion concentration the osmotic pressure increases to a maximum and then diminishes. For 0.5 gram of gelatin in 100 c.c. at  $10^{\circ}$  in univalent acids the maximum osmotic pressure of 158 mm. of water is reached at a hydrogen-ion concentration of  $0.8-1.0 \times 10^{-3}$ . In bases, the maximum pressure of 165 mm. is reached at  $0.2 \times 10^{-3}$  hydroxyl-ion concentration. In bivalent acids or bases ionising as such the maximum osmotic pressure is reached at the same hydrogen- or hydroxyl-ion concentration as with univalent acids or bases respectively, but is only about 55 mm. of water.

When immersed in univalent acids, dry gelatin combines with equivalent amounts at the same hydrogen-ion concentration, and the amount of swelling is approximately the same for all. The maximum swelling occurs at about  $4 \times 10^{-3}$  hydrogen-ion concentration, when one gram of air-dry gelatin occupies a volume of about 46 c.c. Bivalent ionising acids give much less swelling with a maximum at about the same point. Salt-ions do not combine with gelatin, but increase the absorption of alkalis or acids. They markedly decrease swelling and osmotic pressure. The swelling of gelatin is the result of osmotic pressure within the jelly, with the jelly acting as an imperfectly resisting membrane, the more so when highly swollen. Whilst the osmotic pressure at the optimum concentration of univalent acids and bases is the same, the swelling is much less in alkalis because of the weakened membrane effect. Bivalent sulphuric acid gives the same swelling as bivalent calcium or barium hydroxide when swelling is small and the solution is not so great. W. G.

**Digestion of Fibrin and Caseinogen by Trypsin.** EDWARD STAFFORD EDIE (*Biochem. J.*, 1921, **15**, 498-506).—Like alcohol (Edie, A., 1919, i, 460), heat and acids destroy the power of trypsin to digest fibrin more rapidly than its power to digest caseinogen; there seem to be two proteolytic enzymes. The milk coagulating and the proteolytic powers of pancreatic extracts are not in a constant ratio and the former is more thermostable than the latter. G. B.

**Behaviour of Pectin towards Alkalis and Pectase.** FRANK TUTTIN (*Biochem J.*, 1921, **15**, 494—497; cf. von Fellenberg, A., 1915, i, 774).—Pectin was obtained relatively pure in a yield of 9% from dried apple press cake of the cider press. It neutralised in the cold 1.05% of its weight of sodium hydroxide, but on keeping with excess of alkali a further 12.35% of alkali was neutralised in half an hour. On steam distillation some methyl alcohol and about twice as much acetone are given off. The same amounts of methyl alcohol and acetone are liberated by (clover) pectase, and calcium pectate is formed. Alkalis and pectase are therefore quite similar in action. Both reagents produce pectic acid (containing carbon 39.2—39.4%, hydrogen 5.1%, and neutralising 20.9% of sodium hydroxide). G. B.

**The Catalase Reaction.** SERGIUS MORGULIS (*J. Biol. Chem.*, 1921, **47**, 341—375).—All the experiments were performed at 20—21°, using a crude catalase preparation obtained from ox-liver. Preliminary experiments indicated that the catalase reaction diminishes both in velocity and in total decomposition of hydrogen peroxide as the acidity increases, the optimum condition being neutrality ( $P_H$  7.0). All further experiments were therefore performed at  $P_H$  6.7 to 6.9, this slight acidity being maintained to prevent the spontaneous decomposition of the peroxide. Using a constant quantity of catalase, a total volume of 50 c.c., and a peroxide concentration varying from 0.8 to 0.40 molar, it was found that with increasing concentration of peroxide the reaction velocity diminishes, the percentage total decomposition decreases, and the total evolution of oxygen increases to a point and then decreases, the maximum evolution corresponding with a total decomposition of peroxide of 65—70%. With the catalase in excess, 100% decomposition results; when the total decomposition falls below 65—70%, further increases in the amount or concentration of the peroxide cause a falling off of the reaction. Between these limits, however, the total oxygen evolved from a constant quantity of peroxide is directly proportional to the amount of catalase used. For concentrations in which the total decomposition of the peroxide is approximately 70%, the reaction is bimolecular; for a total decomposition of about 95% it is unimolecular. The author concludes that a quantitative relation exists between the catalase and peroxide. Below a total decomposition of 65%, the peroxide exercises a depressing influence, a result which he attributes to a reversible reaction; that it is not due to oxidation of the catalase follows from the experimental results. The bearing of the results on the technique of catalase estimations is finally discussed. E. S.

**Some Additive Compounds derived from Arsines.** GEORGE JOSEPH BURROWS and EUSTACE EBENEZER TURNER (*T.*, 1921, **119**, 148—1450).

**Derivatives of Sulphur in Commercial Salvarsan. II.** HAROLD KING (*T.*, 1921, **119**, 1415—1420).

**Preparation of Arsenic Compounds of the Pyrazolone Series.** FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 313320; from *Chem. Zentr.*, 1921, iv, 262—263).—Acid groups are introduced into the amino-groups of compounds of the type 1-*p*-arsenodiaryl-di(4-amino-2:3-dialkyl-5-pyrazolone). The compounds thus formed, although not markedly poisonous, are strongly bactericidal and may be used in the form of their alkali salts. The products are yellow powders, decomposed by heating with acids. The preparation of some arsenic derivatives of the pyrazolone series is described. 5-Chloro-3-methylpyrazole-1-benzene-4'-arsinic acid is obtained by diazotisation of 5-chloro-3-methylpyrazole-1-*p*-aminobenzene, treatment with arsenites, and subsequent acidification; it forms crystals, m. p. 192—195°, when quickly heated, with the formation of an anhydride and subsequently solidifies on elimination of water; it decomposes completely above 290°. 3-Methyl-5-pyrazolone-1-benzene-4'-arsinic acid is prepared by diazotisation of *p*-aminophenylarsinic acid, reduction, and condensation with ethyl acetoacetate; it crystallises from hot water and forms a yellow nitroso-compound. 2:3-Dimethyl-5-pyrazolone-1-benzene-4'-arsinic acid is formed by the methylation of 3-methyl-5-pyrazolone-1-benzene-4'-arsinic acid or the corresponding 5-chloropyrazole derivative; it crystallises from water. By acting on it with sodium nitrite and dilute sulphuric acid, 4-nitroso-2:3-dimethyl-5-pyrazolone-1-benzene-4'-arsinic acid is obtained; it is bluish-green in colour and very unstable; by reduction, 1-*p*-arsenodiphenyl-di(4-amino-2:3-dimethyl-5-pyrazolone) is obtained. The hydrochloride forms yellow crystals. The monoacetate, prepared by the action of bromoacetic acid, is a yellow powder. With excess of bromoacetic acid, a diglycine is obtained similar to the monoglycine. By the action of formaldehyde sulphonylate on 1-*p*-arsenodiphenyl-di(4-amino-2:3-dimethyl-5-pyrazolone) hydrochloride or 4-nitroso-2:3-dimethyl-5-pyrazolone-1-benzene-4'-arsinic acid, 1-*p*-arsenodiphenyl-di(4-amino-2:3-dimethyl-5-pyrazolone)-monomethylenesulphonylate is obtained as a yellow powder. A dimethylenesulphonylate is obtained when a large excess of formaldehyde sulphonylate is used. By treating 1-*p*-arsenodiphenyl-di(4-amino-2:3-dimethyl-5-pyrazolone) hydrochloride with sodium hydrogen sulphite and formaldehyde the corresponding 4-N-methylsulphinic acid compound is obtained as a yellow powder. G. W. R.

### Physiological Chemistry.

**Respiration and Blood Alkali during Carbon Monoxide Asphyxia.** HOWARD W. HAGGARD and YANDELL HENDERSON (*J. Biol. Chem.*, 1921, 47, 421—431).—The anoxæmia induces excessive breathing (300% or more) which sweeps out the carbon dioxide, and the decrease of blood alkali is an attempt at compensation. After section of the vagi overbreathing and the lowering of the blood alkali do not occur. G. B.

**Relation of the Migration of Ions between Cells and Plasma to the Transport of Carbon Dioxide.** EDWARD A. DOTY and EMILY P. EATON (*J. Biol. Chem.*, 1921, 47, 377—393).—The authors have determined the sodium, potassium, chlorine, phosphorus, and bicarbonate content of serum, obtained by centrifuging defibrinated blood, which had been equilibrated with various pressures of carbon dioxide. They find it quite easy to show that increased carbon dioxide content of the plasma produces a shift of hydrochloric acid into the corpuscles; this is what happens during the passage of the blood through the capillaries; since oxygen is given up by the hæmoglobin, the latter becomes less acid and compensates for the hydrochloric acid migrating into the corpuscles. Perhaps phosphate ions also migrate, but the concentration of these and of the sulphuric ions is so small as to make their shift unimportant. Contrary to Hamburger, the authors failed to detect any shift of sodium or potassium, and they regard the blood cells as impermeable to these ions, in agreement with Collip (this vol., i, 379). A tabulation of total molecular concentrations of anions and cations in serum shows an excess of 7% of bases, presumably combined with the protein. G. B.

**Distribution of Calcium and Phosphoric Acid in the Blood of Normal Children.** MARTHA R. JONES and LILLIAN L. NYE (*J. Biol. Chem.*, 1921, 47, 321—331).—Estimations were made of the alkali reserve of the plasma, and of the distribution of calcium and phosphoric acid in the blood of children. More phosphoric acid of all types was found in the corpuscles than in the plasma. The unknown phosphoric acid is approximately 70% of the total in the corpuscles, but is negligible in or absent from the plasma. The average calcium content of the corpuscles is slightly less than that of the plasma. E. S.

**Mechanism of Anticoagulant Actions [in Blood Clotting].** ANDRÉ GRATIA (*Ann. Inst. Pasteur*, 1921, 35, 513—557).—The author has been principally concerned with the anticoagulant action of the antithrombins of hirudin and of plasma after peptone injection, and his results support the theory of Schmidt, Morawitz, Bordet, and Delange, rather than those of Nolf and of Howell. Whereas a hirudin solution of 1 : 2500 may be required to prevent the action of ready formed thrombin, a solution of 1 : 10000 will suffice to prevent the activation of prothrombin by kinase. Neutral thrombin-antithrombin mixtures are decomposed at 60° with liberation of antithrombin. This is true of both hirudin and peptone plasma, which differ, however, in other respects (cf. also Dale and Walpole, A., 1916, i, 889). G. B.

**The Diffusible Calcium of the Blood Serum. I. Estimation.** L. VON MEYSENBUG, A. M. PAPPENHEIMER, T. F. ZUCKER, and MARJORIE F. MURRAY. **II. Human Rickets and Experimental Dog Tetany.** L. VON MEYSENBUG and G. F. MCCANN (*J. Biol. Chem.*, 1921, 47, 529—539, 541—546).—The authors have confirmed the observations of Rona and Takahashi (A., 1911, ii, 302)

and of Cushny (A., 1920, i, 508) that 30—40% of the calcium in serum is non-diffusible; this percentage is not changed by altering the carbon dioxide saturation of the serum between 17 and 62 mm. Although, as Howland and Marriott (*Quart. J. Med.*, 1917, **11**, 289) have shown, there is a slight diminution in the calcium content of serum in rickets, the percentage of non-diffusible calcium here remains normal, and the same applies to the greater diminution in calcium during tetany, after removal of the parathyroids, as observed by MacCallum and Voegtlin (*J. exp. Med.*, 1909, **11**, 118). The method of analysis is by compensatory dialysis. G. B.

**Animal Calorimetry. XVII. The Influence of Colloidal Iron on the Basal Metabolism.** EINAR LANGFELDT (*J. Biol. Chem.*, 1921, **47**, 557—563).—Intravenous injection of negative ferric hydroxide sol (Fischer, A., 1910, ii, 856) in dogs increased the heat production by 7—15%, increased the oxygen consumption and carbon dioxide output, and slightly increased the respiratory quotient. The chief increase of the total heat production falls in the non-protein metabolism. G. B.

**The Metabolism of Nitrobenzaldehydes and Nitrophenylacetaldehyde.** CARL P. SHERWIN and WALTER A. HYNES (*J. Biol. Chem.*, 1921, **47**, 297—301).—After ingestion by man, *o*-, *m*-, and *p*-nitrobenzaldehydes and *p*-nitrophenylacetaldehyde were largely recovered from the urine in the form of the corresponding carboxylic acids. The *m*- and *p*-nitrobenzaldehydes were also, to some extent, excreted as nitrohippuric acid. In no case was reduction of the nitro-group observed. E. S.

**Antiketogenesis. I. An *in vitro* Analogy. II. The Ketogenic-Antiketogenic Balance in Man.** PHILIP A. SHAFFER (*J. Biol. Chem.*, 1921, **47**, 433—448, 449—473).—Dextrose, lævulose, and glycerol (but not lactic acid) greatly increase the rate of oxidation of acetoacetic acid by hydrogen peroxide at room temperature. Evidently a chemical reaction occurs between some derivative of dextrose and acetoacetic acid, involving definite molecular quantities of each substance.

This "ketolytic" action *in vitro* is similar to the long-known "antiketogenic" action of carbohydrates in preventing the appearance of acetone substances in man. Using mainly experimental data of others, the author calculates the amount of acetoacetic acid which might be produced from the fatty acid and protein of various diets and finds that the minimum molecular ratio of ketogenic to antiketogenic substances for the avoidance of ketonuria (and  $\beta$ -hydroxybutyric acid) is unity. For a case of "total" diabetes with extreme acidosis, the author is enabled to calculate from the diet with fair accuracy the amount of  $\beta$ -hydroxybutyric acid actually excreted. G. B.

**Chemical Examination of the Amniotic Fluid.** R. CLOGNE and J. RÉGLADE (*Bull. Soc. Chim. Biol.*, 1921, **3**, 279—282).—The results are given of a number of estimations of urea in the amniotic fluid, and in the urine of new-born children. No parallelism between

the two is found, the concentration in the urine being much the higher. Examination of the amniotic fluid for ferments (oxydases and reductases) gave negative results. C. R. H.

**Odoriferous Substances and the Sense of Smell.** A. TSCHIRCH (*Schweiz. Apoth. Zeit.*, 1921, 59, 229—232, 241—246, 254—258, 265—272; from *Chem. Zentr.*, 1921, iii, 190—191).—A theoretical discussion of the relationships between odour and chemical constitution and also of the mechanism of odour-perception. Whilst quality of odour cannot be correlated with chemical constitution, yet certain groups appear to be connected with intensity of odour. The odour of a substance depends on its solubility in air and also on its partition coefficient between air and the lipid plasma of the olfactory cells. The sensation of smell is probably due to the formation of loose compounds of the odoriferous substance with the olfactory cell plasma and is thus a chemical stimulus. G. W. R.

**Lipase. I. The Hydrolysis of the Esters of some Dicarboxylic Acids by the Lipase of the Liver.** ADAM A. CHRISTMAN and HOWARD B. LEWIS (*J. Biol. Chem.*, 1921, 47, 495—505).—The lipase from pig's liver eliminates only one ethyl group from ethyl succinate and ethyl malonate. Ethyl hydrogen malonate was probably isolated. This and potassium ethyl malonate are not attacked by the lipase. G. B.

**Effect of Hydrochloric Acid Ingestion on the Composition of the Urine in Man.** RAYMOND L. STEHLE and ARTHUR C. McCARTY (*J. Biol. Chem.*, 1921, 47, 315—319).—The ingestion of hydrochloric acid causes an increased excretion of potassium, sodium, ammonia, phosphoric acid, and hydrogen ions in the urine. E. S.

**Urobilin and Stercobilin [in the Urine] of Infants.** MARCEL BRULÉ and H. GARBAN (*Compt. rend. Soc. Biol.*, 1921, 84, 482—483; from *Chem. Zentr.*, 1921, iii, 184).—In the examination of urines, when urobilinogen is changed into urobilin the oxidation is generally carried too far, so that urobilin is decomposed. The authors recommend the addition to 10 c.c. of urine of a small quantity of zinc acetate and an equal volume of 95% alcohol. The liquid is filtered after half an hour and tested by means of fluorescence. Urine of newly-born infants, of high density, contains much urobilin; in urine of lower density urobilin is detected with difficulty. There is no correlation between the urobilin content of the urine and the appearance of stercobilin. Urobilin may be found considerably before stercobilin appears. Urobilin in the newly born is formed from the blood pigment and is due to hyperhemolysis. These facts contradict the "enterohepatic" theory of urobilinuria. G. W. R.

**Pyrrrole and Melanuria. IV.** P. SACCARDI (*Gazzetta*, 1921, 51, 108—112; cf. this vol., i, 203, 790).—2:5-Dimethylpyrrrole has been examined by the author as a possible source of melanin. It is found that, *in vitro*, this compound does not yield melanin, whereas, when introduced hypodermically into the animal

organism, it undergoes profound modification, being certainly demethylated and probably carboxylated by oxidation of the methyl groups; it seems likely that the pyrrole ring is connected by means of the carboxyl groups with the remainder of the melanogen molecule.

2:5-Dimethylpyrrole is readily ingested and is eliminated only very slowly, the urine becoming slightly melanotic. Enzymic oxidation *in vitro* is insufficient to transform it into melanogen or melanin.

T. H. P.

#### The Degradation of *n*-Valeric Acid in the Animal Organism.

L. BLUM and E. AUBEL (*Bull. Soc. Chim. Biol.*, 1921, **3**, 307—310).—The authors have isolated *d*-lactic acid and pyruvic acid from the urine of rabbits after intravenous injection of an aqueous solution of the sodium salt of *n*-valeric acid.

C. R. H.

#### Pharmacology of Acridine and Acridinium Compounds.

EMIL LENZ (*Zeitsch. ges. exp. Med.*, **12**, 195—261; from *Chem. Zentr.*, 1921, iii, 188—189).—The pharmacology of the following compounds was investigated: 3:6-diaminoacridinium chloride; 3:6-diamino-10-methylacridinium chloride ('trypaflavine'); 3:6-diamino-2:7-dimethylacridine ('acridine-yellow'); 3:6-diamino-2:7:10-trimethylacridinium nitrate ('brilliant phosphine nitrate'); 3:6-diaminodimethyl-2:7:10-trimethylacridinium nitrate ('brilliant iminophosphine'); the silver double salt of trypaflavine ('argoflavine'); and 'septacrol' (additive product of silver nitrate and 'brilliant phosphine nitrate').

'Trypaflavin' in 0.005*N*-solution is immediately fatal to protozoa, and exerts an effect even in 0.00025*N*-solution. 'Brilliant iminophosphine' is somewhat stronger and 'acridine yellow' slightly weaker in effect. 'Trypaflavine' and 'brilliant iminophosphine' induce motor and respiratory paralysis, inhibition of reflexes, central paralysis, and finally cardiac failure in frogs. The lethal dose is 0.8—1 milligram per gram live weight in the case of 'trypaflavine' and 0.54 milligram in the case of 'brilliant iminophosphine.' With warm-blooded animals (mice, guinea pigs, and rabbits) these compounds are correspondingly poisonous.

The respiratory paralysis caused by large doses is consequent on central paralysis. One-third to one-half of the fatal dose causes transitory respiratory disturbances, whilst with somewhat larger doses a stage of excitement is reached. The circulation is affected when the respiratory paralysis is advanced. Other experiments showed that this effect is not secondary, but was due to a direct action on the vascular system. In frogs, the heart is a point of attack of the poison. Finally, peripheral vascular paralysis also occurs. In rabbits and guinea-pigs local irritation of the cornea together with 'acridine leucocytosis' occurred. After lethal doses, all organs show a yellow coloration. The compounds are found in the urine immediately after intravenous or subcutaneous injection. Only traces of the poison are found in the spinal fluid. 'Brilliant iminophosphine' is more poisonous than 'trypaflavine.'

G. W. R.

**Experimental Rickets in Rats. II. The Failure of Rats to develop Rickets on a Diet Deficient in Vitamin-A.** A. F. HESS, G. F. McCANN, and A. M. PAPPENHEIMER (*J. Biol. Chem.*, 1921, 47, 395—409).—The authors do not confirm E. Mellanby's view, that the cause of rickets is a deficiency of the fat-soluble vitamin. G. B.

**Experimental Rickets. VIII. Production of Rickets by Diets Low in Phosphorus and Fat-soluble-A.** E. V. McCOLLUM, NINA SIMMONDS, P. G. SHIPLEY, and E. A. PARK (*J. Biol. Chem.*, 1921, 47, 507—527).—Rickets (in rats) is not simply due to a deficiency of vitamin-A, as suggested (for dogs) by E. Mellanby. To produce rickets, the calcium:phosphorus ratio of the diet must be upset, making its calcium content relatively high, its phosphorus content low. With a calcium:phosphorus ratio differing from the optimal for normal ossification, rickets may still be avoided by giving an antirachitic substance such as cod-liver oil. The ratio of calcium:phosphorus is of "infinitely greater importance" in ensuring normal ossification than the absolute amounts of these elements in the diet. G. B.

## Chemistry of Vegetable Physiology and Agriculture.

**Pressure developed by Alcoholic Fermentation.** R. KOLK-WITZ (*Ber. Deut. bot. Ges.*, 1921, 39, 219—223).—Although the viability of yeasts and other micro-organisms is not affected by pressures amounting to thousands of atmospheres and yeast-cells occur and vegetate normally in marine oozes under pressures of more than thirty atmospheres, the pressure developed by the evolution of carbon dioxide in alcoholic fermentation is generally estimated as little more than twelve atmospheres. Working with a specially constructed apparatus, the author was able to obtain a pressure of forty atmospheres by fermentation for three to five hours. The gradual slowing down of the evolution of carbon dioxide which was observed is attributed to narcosis by the dissolved gas rather than to the direct effect of the pressure produced. Microscopic examination showed that the older yeast-cells which had been exposed to high pressure had suffered injury by contraction of their protoplasmic contents. The younger cells appeared homogeneous. Placed in a fresh nutrient solution under normal pressure, fermentation took place relatively slowly at first. The experiments show that yeast fermentation is possible under relatively high pressures, and that it is not necessary to assume the existence of yeast organisms specially adapted to high pressures in the greater depths of the sea. G. W. R.

**Production of Glycerol by Alcoholic Fermentation.** K. SCHWEIZER (*Chim. et Ind.*, 1921, 6, 149—159).—The author



discusses the mechanism of alcoholic fermentation of sugars and the formation of glycerol among the accessory products of the action. A summary is given of the methods by which the normal course of fermentation has been modified in order to produce glycerol.

G. W. R.

**Vitamin Content. II. The Yeast Test as a Measure of Vitamin-B.** WALTER H. EDDY, HATTIE L. HEFT, HELEN C. STEVENSON, and RUTH JOHNSON (*J. Biol. Chem.*, 1921, **47**, 249—275).—Confirmatory evidence is produced showing that the yeast test is not a quantitative measure of vitamin-B content. It is possible, however, that the presence of vitamin-B is one of the factors causing the stimulation of the growth of yeast by vegetable extracts (cf. Fulmer, Nelson, and Sherwood, this vol., i, 292; Nelson, Ellis, Fulmer, and Cessna, *ibid.*, i, 386; MacDonald and McCollum, *ibid.*, i, 480).

E. S.

**Oligodynamy. Activation of Water by Copper and its Oxides.** RAUL WERNICKE and ALFREDO SORDELLI (*Anal. Asoc. Quím. Argentina*, 1921, **9**, 145—182).—The authors give a comprehensive review of previous work on the subject of oligodynamy. In order to determine whether the activation of water is due to solution of the activating substance, the behaviour of copper was studied. As a reagent for detecting the presence of copper at great dilutions, an aqueous solution containing *p*-phenylenediamine,  $\alpha$ -naphthol, and sodium hydroxide was used. The bactericidal action of the waters obtained was tested on cultures of paratyphus-A. The results showed that activation was always accompanied by solution of copper, and that when no solution took place water was not activated. Activation was not produced in the case of water distilled in an atmosphere of oxygen or hydrogen. The presence of both oxygen and carbon dioxide would appear to be necessary for activation to take place. It was shown that water containing 1:3,000,000 of copper had a bactericidal action. The efficacy of such dilute solutions is explained by assuming colloidal adsorption of the dissolved substance by the organism. G. W. R.

**The Rôle of Osmotic Pressure in the Toxicity of Soluble Salts.** J. E. GREAVES and YEPPA LUND (*Soil Sci.*, 1921, **12**, 163—181).—The effect of chlorides, sulphates, carbonates, and nitrates of potassium, sodium, calcium, magnesium, iron, and manganese when added to soils in varying quantities, on the osmotic pressure and on ammonifying and nitrifying organisms was determined. With the exception of manganese nitrate, iron nitrate, and sodium carbonate there was a close correlation between toxicity and osmotic pressure. There is, however, probably also a physiological action of the salts in the living protoplasm such that it cannot function normally.

W. G.

**The Respiration of Leaves in a Vacuum or in Atmospheres Poor in Oxygen.** L. MAQUENNE and E. DEMOUSSY (*Compt. rend.*, 1921, **173**, 373—378).—The length of time during which

leaves will remain alive in the dark in atmospheres poor in oxygen depends on the absolute amount of oxygen present rather than its relative pressure. The small amount of oxygen, which results from the decomposition of the respiratory carbon dioxide by the chlorophyll function, in light, is sufficient for the leaf during the night. Normal respiration is absolutely essential for the maintenance of plant life. Intracellular and normal respiration proceed from different causes, and must be regarded as autonomous functions, as much by their intimate mechanism as by their influence on the life of green plants. W. G.

**Composition of Gases in the Intercellular Spaces of Apples and Potatoes.** J. R. MAGNESS (*Bot. Gaz.*, 1920, **70**, 308—316; from *Chem. Zentr.*, 1921, iii, 175).—With rise of temperature the amount of carbon dioxide increases, whilst the amount of oxygen decreases to a smaller extent. G. W. R.

**The Resistance of Plants to Asphyxia.** L. MAQUENNE and E. DEMOUSSY (*Bull. Soc. Chim. Biol.*, 1921, **3**, 273—278).—Germination can follow a normal course in seeds which are immersed in water, provided that the latter contains dissolved oxygen. Green leaves will survive for a considerable period in circulating water, and in stagnant water if exposed to sunlight; they will also live for several days in a vacuum tube, if exposed to the sun during the daytime. C. R. H.

**The General Presence of Manganese in the Vegetable Kingdom.** GABRIEL BERTRAND and (MME) M. ROSENBLATT (*Compt. rend.*, 1921, **173**, 333—336).—It is shown that the various plants and parts of plants which Maumené reported as devoid of manganese (cf. *Compt. rend.*, 1884, **98**, 1416) do without exception contain manganese. Thus the presence of manganese is general in all the organs and species of the vegetable kingdom. W. G.

**The Distribution of Iron in Plants.** L. MAQUENNE and R. CERIGHELLI (*Compt. rend.*, 1921, **173**, 273—278).—Iron enters only to a comparatively slight extent into the composition of plant tissues. In general its distribution in plants is comparable with that of copper (compare Maquenne and Demoussy, A., 1920, i, 270), the young organs, buds or leaves, containing more than the old ones. Like copper, it is capable of migrating in plant tissues, tending to move towards the centres of active life and reproduction. W. G.

**Extraction and Nature of the Hydrosulphide Compound in the Seeds of certain Papilionaceae.** MARCEL MIRANDE (*Compt. rend.*, 1921, **173**, 252—253).—The substance present in the seeds of *Lathyrus* and other *Papilionaceae*, which by autofermentation in contact with water gives rise spontaneously to hydrogen sulphide, is apparently a protein which thus loses the labile sulphur which it contains. W. G.

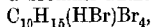
**Constituents of the Root of Gishi-gishi.** YOSHIMARU MURAYAMA and TAKEKI ITAGAKI (*J. Pharm. Soc. Japan*, 1921, 327—330).—From a hot alcoholic extract of the dried root of gishi-gishi (*Rumex crispus*, L. var. *japonicus*, Makino), the authors isolated 0.12% of frangula-emodin,  $C_{15}H_{10}O_5$ , orange-red prisms, m. p. 250—252°, and 0.5% of chrysophanic acid, this being partly free in the extract and partly combined with sugar.

K. K.

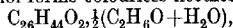
**The Existence of Anthocyanidins in the Free State in the Fruits of *Ruscus aculeatus* and *Solanum Dulcamara*.** ST. JONESCO (*Compt. rend.*, 1921, 173, 168—171).—Anthocyanidins exist in the free state in the fruits of *Ruscus aculeatus* and *Solanum Dulcamara*, picked in July before they were fully ripe. They are found along with anthocyanins in the red pigment which gives the colour to the fruit.

W. G.

**Japanese Birdlime.** HIDEKICHI YANAGISAWA (*J. Pharm. Soc. Japan*, 1921, No. 471, 405—423).—Japanese birdlime is of two kinds. The best, which is red, is made from the bark of *Trochodendron aralioides*, whilst the white one (common kind) is prepared from many kinds of *Ilex* and related plants (cf. *Bot. Mag.*, 28, Nos. 229 and 230). By the saponification of the red variety with alcoholic potash, palmitic acid, resin, and a neutral unsaponifiable crystalline substance, *trochol*, were isolated. A caoutchouc, a slightly brown mass, which gave a bromine additive compound,



was also obtained. After purification by precipitation from chloroform solution by light petroleum and recrystallisation from chloroform-alcohol, trochol forms colourless needles or prisms,



m. p. 252°,  $[\alpha]_D^{25} + 20^\circ$  (in chloroform-alcohol). It yields a *diacetate*, colourless needles or prisms, m. p. 217°, from which by treatment with bromine, a bromo-derivative,  $C_{26}H_{40}Br_2(OAc)_2$ , m. p. 293°, was obtained although trochol itself gave no definite bromine compound. The *dibenzoate* of trochol forms colourless needles, m. p. 172° (sintering at 145°); the *monobenzoate* forms colourless leaves, m. p. 282°. Trochol seems to occur as the palmitic ester in the birdlime, and by heating the two components at 200° in a vacuum, the ester was produced as a colourless, viscous substance. *Trochol cinnamate* was prepared by the same method as yellow, lustrous crystals, m. p. 155°, after sintering at 132°.

From the white birdlime, by saponification with alcoholic potash, an alcohol,  $C_{26}H_{48}OH$ , m. p. 222°, was prepared, which gave an acetate, m. p. 203°. All the properties of the alcohol correspond with the mochl alcohol of Divers and Kawakita (*T.*, 1888, 53, 268).

K. K.

## General and Physical Chemistry.

**Balmer Series of Hydrogen.** E. GEHRCKE and E. LAU (*Ann. Physik*, 1921, [iv], 65, 564—576).—The lines of the Balmer series of the hydrogen spectrum have been examined with respect to their structure, energy partition, and width. It is shown that the Balmer lines are more easily obtained in the presence of a little water. The intensity relationship of the two components is found to depend on the method of excitation and the source of light.

J. F. S.

**Mass Spectra of the Alkali Metals.** F. W. ASTON (*Phil. Mag.*, 1921, [vi], 42, 436—441).—An apparatus for the production of positive rays of the alkali metals by volatilising their salts by means of a hot anode is described. The following results were obtained :

Element.	Lithium.	Sodium.	Potassium.	Rubidium.	Cæsium.
Minimum number of isotopes . . . .	2	1	2	2	1
Mass of isotopes in order of intensity .	7, 6	23	39, 41	85, 87	133

It is shown that for the great majority of the possible configurations even atomic weight is associated with even atomic number and odd with odd, which is interpreted as meaning that in the nuclei of most types of atoms the number of electrons is an even number.

J. R. P.

### Quantitative Relationships of the Cæsium Spectrum.

HANS BARTELS (*Ann. Physik*, 1921, [iv], 65, 143—166).—The series now put forward by Fichtbauer and Hoffmann (*Ann. Physik*, 1914, 3, 96) has been examined in the case of the cæsium doublet  $5p$  ( $\lambda=3612$  and  $3617$ ) and found to be correct within the limits of experimental error. The absorption of the strongest component ( $\lambda=3612$ ) of the principal series doublet  $5p$  has been measured and by making use of earlier measurements has been compared with the absorption of the corresponding component of the doublet  $4p$ . From the absorption measurements by means of the Herz vapour pressure formula  $\log_e p = A + B \log_e T + c/T$ , several values of the vapour pressure of cæsium have been calculated. These values are:  $190.9^\circ$ ,  $p=0.046$  mm.,  $199.2^\circ$ ,  $p=0.068$  mm.,  $204.7^\circ$ ,  $p=0.084$  mm.,  $232.3^\circ$ ,  $p=0.211$  mm. (cf. Kröner, A., 1913, ii, 383). These values probably have a 10% absolute error, and a relative error of 4%.

J. F. S.

**Bergmann Series of Cæsium.** K. W. MEISSNER (*Ann. Physik*, 1921, [iv], 65, 378—392).—The vacuum arc spectrum of cæsium has been photographed and evaluated in the red and infra-red regions. Twenty-nine lines of wave-lengths 8079–9021—6010–489 Å.U. are recorded, the values of which were obtained by reference to the red cadmium line  $2p_2-4.5s$ , 6354.552 Å.U. The

measured lines are used for the investigation of the Bergmann series. It is shown that various pairs have not a constant frequency difference, but the individual components come more closely together the larger the series number, and for the series number  $m=\infty$  the difference  $\Delta\nu$  reaches the limiting value 97.59  $\text{cm}^{-1}$ . The two limiting terms necessary to characterise the series are found to be 16809.620 ( $3d_1$ ) and 16907.190 ( $3d_2$ ). Making use of these limiting values, the wave-lengths calculated and observed are compared and a remarkably good agreement is obtained.

J. F. S.

**Arc and Spark Spectra of the Alkalis, Alkaline Earths, and Earths.**

R. SEELIGER and D. THAER (*Ann. Physik*, 1921, [iv], 65, 423—448).—The arc and spark spectra of lithium, sodium, potassium, magnesium, calcium, zinc, mercury, and aluminium have been investigated. It is shown in all these cases that the displacement law is correct in so far as all the lines of the elements may be arranged in two groups of smaller and larger exciting energy. The energy necessary for the excitation of the arc lines increases from the alkalis to the earths through the alkaline earths. The energy necessary for excitation of the arc lines of one and the same element increases in the order: Bergmann series, principal series, second subsidiary series, first subsidiary series, single line series, spark lines. The unknown form of the excitation function has considerable influence in both the above cases. It is significant that in its entire behaviour the Bergmann series, of the whole arc series, is furthest removed from the spark lines. The spark spectrum (fundamental spectrum) of sodium has been observed in the negative glow of the glow discharge. The results concerning the intensity relationships at the edge of the glow discharge show that the exciting energy of the single line series is greater than that of the remaining arc series. Vigorous evaporation of the cathode in a glow discharge is not generally sufficient to lower the cathode potential to that characteristic lower value required for the arc, but an anomalous cathode fall may be set up over a vaporising molten cathode.

J. F. S.

**Absorption of Light by Elements in a State of Vapour. The Halogens.**

(SIR) J. J. DOBBIE and J. J. FOX (*Proc. Roy. Soc.*, 1921, [A], 99, 456—461; cf. A., 1920, ii, 170).—The absorption of light by iodine and bromine vapour and by chlorine has been examined at temperatures from 22° to 1350°. When light from a Nernst filament is allowed to fall on a white screen after passing through bromine vapour at various temperatures it is found that the colour, which is deep orange at ordinary temperatures, changes to brick red at 100°, the intensity of the transmitted light diminishes at 600° and above, and the vapour is most opaque at 900°. Above this point the colour changes to orange-red; at 1200° it is pale yellow, and at still higher temperatures nearly white. The absorption increases regularly up to about 900° and then falls off continuously. The absorption band has its middle situated at about  $\lambda 4170$ . Iodine vapour changes colour on heating,

at temperatures up to  $300^{\circ}$  the colour being reddish-violet, which deepens in shade up to  $500^{\circ}$ . At this temperature, the intensity of the transmitted light is much enfeebled and remains so to  $800^{\circ}$ , when it again increases, the violet shade becoming lighter. At still higher temperatures, the violet shade passes gradually into a bright salmon colour, and finally disappears almost entirely. The absorption increases regularly to  $600^{\circ}$ , and is much more distinctly defined than in the case of bromine. In the case of chlorine, the absorption becomes greater with increase of temperature up to  $1190^{\circ}$ , but up to this temperature no reversal is observed as in the other cases. The results are discussed in connexion with the dissociation and size of the molecules of the halogens. J. F. S.

**Colorations produced by Substituted Nitroforms.** HUGH GRAHAM and ALEXANDER KILLEN MACBETH (T., 1921, 119, 1362—1368).

**Criticism of Bohr's Theory of Light Emission.** A. SOMMERFELD (*Jahrb. Radioaktiv. Elektronik*, 1921, 17, 417—429).—The author supports Bohr's theory against criticisms of J. Stark (this vol., ii, 232). J. R. P.

**Significance of Continuous Absorption and Emission Spectra in Bohr's Theory.** R. LADENBURG (*Jahrb. Radioaktiv. Elektronik*, 1921, 17, 430—434).—Polcmical with J. Stark (see preceding abstract). J. R. P.

**Luminescence of Solid Solutions.** GERHARD C. SCHMIDT (*Ann. Physik*, 1921, [iv], 65, 247—256).—The author has examined the luminescence of a number of dyes adsorbed in other material and finds that in no case is any fluorescence to be observed; on the other hand, the same dyes when in solid solution in gelatin or phthalic acid exhibit a very pronounced fluorescence. Among the dyes examined were bismarck-brown, quinoline-yellow, congo-red, ponceau-red, eosin, methylene-blue, and methyl-violet. The difference noted above can be shown with one and the same substance as solvent or adsorbent; thus benzoic acid in which methyl-violet is adsorbed shows no fluorescence, whilst when the methyl-violet is dissolved in the acid to form a solid solution a very intense yellowish-red fluorescence is observed. It is shown further that the fluorescence of fluorescein, eosin, and fluoridin in benzidine, benzoic acid, phthalic acid, acetamide, benzamide, and acetanilide is the same in both liquid and solid solutions. The adsorption of methyl-violet in benzoic acid from aqueous solution follows the partition law. The author attributes the different behaviour in the two cases to the different condition of the dye substance; in the case of adsorption, the dye lies on the surface, but in the case of solid solutions the dissolved substance lies in the crystal lattice of the solvent. The difficulty of formation of solid solutions in inorganic substances is considered and explained. J. F. S.

**Active Racemic Substances.** MARCEL DELÉPINE (*Bull. Soc. chim.*, 1921, [iv], 29, 656—669).—A discussion of the literature on

this subject, in which the author adopts the more general definition of a racemic compound as a crystalline edifice composed of molecules of dextrorotatory configuration and of levorotatory configuration in equal numbers. Optical activity is only an accessory phenomenon dependent on the quality of each molecule. This is amplified by illustrations showing the possibility of obtaining active racemic compounds.

W. G.

**Temperature Coefficient of the Electrical Double Refraction in Liquids.** II. C. BERGHOLM (*Ann. Physik*, 1921, [iv], 65, 128—142; cf. *ibid.*, 1916, 51, 414).—The temperature coefficient of the electrical double refraction has been determined, by the method previously adopted, for the liquids: toluene, *m*-xylene, carbon disulphide, chlorobenzene, bromobenzene, chloroform, ethyl ether, ethylene dibromide, and carbon tetrachloride. It is shown that the agreement between the observed and calculated values of the temperature coefficient is only qualitative. The relationship,  $B_T/B_{20}$ , between the Kerr constant at  $t^\circ$  and  $20^\circ$  in the case of toluene and carbon disulphide is very nearly dependent on the wave-length of the light used. In the case of liquids with a more positive Kerr constant,  $B_T$ , the expression  $B_T/(\epsilon+2)^2$  is very nearly constant,  $\epsilon$  being the dielectric constant at  $t^\circ$ .

J. F. S.

**New Application of Einstein's Photochemical Equivalent Law.** WALTER NODDACK (*Zeitsch. Elektrochem.*, 1921, 27, 359—364).—The photochemical reactions between bromine and cyclohexane and between chlorine and trichlorobromomethane have been investigated. In the former case a slow, dark reaction takes place; in the latter no recognisable change takes place in forty days at  $37^\circ$ , but some reaction occurs at  $100^\circ$  in several hours (see this vol., ii, 580). It is shown that both reactions follow the Einstein photochemical equivalent law, the divergences observed being explained by the experimental error and by the complicated dark reaction. In the case of the reaction between chlorine and trichlorobromomethane, it is found that admixture with carbon tetrachloride lowers the photochemical effect with increasing dilution. This phenomenon is ascribed to the energy loss of the activated molecules owing to indifferent collisions with the carbon tetrachloride molecules. The illumination of the mixture: chlorine, trichlorobromomethane, carbon tetrachloride, represents a limiting case of pure photochemistry and in it the light energy is partly converted into chemical energy and partly into heat. The life of the Bohr condition has been deduced from the decrease of the photochemical effect, and is found to be approximately  $10^{-9}$  seconds.

J. F. S.

**Photographic Colloid-Chemical Crystallisation Processes.** A. STEIGMANN (*Kolloid Zeitsch.*, 1921, 29, 145—148; cf. this vol., ii, 13, 147).—A theoretical paper in which the author discusses the results obtained in previous papers (*loc. cit.*).

J. F. S.

**Passivity and Photo-electricity.** WILHELM FRESE (*Zeitsch. wiss. Photochem.*, 1921, 21, 37—44).—The connexion between passivity and the photoelectric sensitiveness of metals has been examined (Allen, A., 1913, ii, 172). It is shown that the photoelectric sensitiveness of iron, zinc, and aluminium is greatly reduced after treatment with alcohol or water. In the case of copper, cobalt, nickel, silver, gold, and palladium, a similar treatment brings about only the slightest reduction of the photoelectric sensitiveness; in the case of platinum there is no change at all. All oxidising agents, which render iron, nickel, and cobalt passive, strongly reduce the photoelectric sensitiveness, whilst reducing agents, particularly nascent hydrogen, increase it. The above action is more intense the longer the reagents remain in contact with the metal. The same phenomenon is observed in the case of platinum and palladium, and also in metals which do not become passive, proving that the parallelism between passivity and photoelectric sensitiveness as found by Allen (*loc. cit.*) is incorrect. In the case of gold, silver, zinc, copper, and aluminium, the photoelectric sensitiveness is greatly reduced by oxidising agents and increased by reducing agents. The above results are explained as follows. The reduction of the photoelectric sensitiveness of iron, aluminium, and zinc by treatment with alcohol or water is attributed to the formation of a thin film of oxide. That no such action occurs in the case of the nobler metals is due to the greater difficulty experienced in oxidising these elements. The great increase in the photoelectric sensitiveness brought about by hydrogen points to the fact that hydrogen is the carrier of photoelectric sensitiveness. That all metals when charged with hydrogen become strongly photoelectric supports this view. J. F. S.

**X-Ray Bulb with Liquid Mercury Anticathode and Wave-Length Measurements of the L-Spectrum of Mercury.** ALEX MÜLLER (*Phil. Mag.*, 1921, [vi], 42, 419—427).—An arrangement is described in which an anticathode of liquid mercury is bombarded by cathode rays for the production of the X-ray spectrum. The wave-lengths of 14 lines in the L-spectrum are given, varying from 834.8—1418.3 ( $\times 10^{-11}$  cm.). J. R. P.

**Effect of the Rays from Radium, X-Rays, and Ultra-violet Rays on Glass.** J. R. CLARKE (*J. Soc. Glass Technology*, 1921, 5, 155—165).—A series of soda-lime glasses of the same composition, except that some contained selenium, some cobalt oxide, and others no admixture, have been exposed to the action of  $\alpha$ -,  $\beta$ - and  $\gamma$ -rays,  $\beta$ - and  $\gamma$ -rays,  $\gamma$ -rays, X-rays, and ultra-violet rays respectively. All glasses containing selenium or cobalt oxide were coloured brown by  $\beta$ -rays, the depth of coloration corresponding with the range of the  $\beta$ -particles in the glasses. The intensity of coloration was greatest at the surface, decreased toward the interior, and increased with increasing selenium or cobalt oxide content. As the radiation was prolonged, the intensity increased to a maximum which depended on the percentage of colouring agent, and then remained constant. The pure soda-lime glass was only affected by  $\alpha$ -rays,



being faintly coloured on the surface only. None of the glasses were affected by X-rays,  $\gamma$ -rays, or ultra-violet rays. All the glasses fluoresced in radium emanation, but a fatigue effect was observed at about the same time as the attainment of maximum intensity of coloration. The coloration of glasses is regarded as due to the formation of colloidal particles in the glass. The presence of such particles is explained as being due to the action of  $\alpha$ - or  $\beta$ -rays on ions already present in the glasses. The fluorescence is held to be due to mechanical bombardment of the glass molecules by the rays.

J. F. S.

**Soft Characteristic X-Rays from Arcs in Gases and Vapours.** F. L. MOHLER and PAUL D. FOOTE (*J. Washington Acad. Sci.*, 1921, **11**, 273—274).—If an electron current is maintained by a potential  $V$  between a hot cathode and anode in a vapour at low pressure, successive changes in the spectrum excited by electron impact occur, as  $V$  is increased. The maximum frequency of each additional group of lines,  $\nu$ , is related to the minimum exciting potential by the quantum equation  $Ve=hc\nu$ . The stages in the discharge were studied by measuring the photoelectric effect of the radiation on two other electrodes entirely shielded from ions produced in the arc. The photoelectric current plotted as a function of the exciting voltage shows nearly a linear relation with changes of slope at critical potentials. In this way potentials are found which are determined by the limiting frequency of the softest X-ray series of sodium, magnesium, phosphorus, sulphur, chlorine, carbon, nitrogen, and potassium. A new X-ray series of feeble intensity was detected.

J. R. P.

**Nickel Isotopes.** F. H. LORING (*Chem. News*, 1921, **123**, 81).—Certain modifications in previous calculations (see A., 1920, ii, 171) are made in view of the announcement of the existence of isotopes of nickel, of atomic weights 58 and 60, by Aston (*Nature*, 1921, **108**, 520).

J. R. P.

**Variation of Resistance of Selenium with Temperature.** SNEHAMOY DATTA (*Phil. Mag.*, [vi], **42**, 463—470).—The change of resistance of selenium with temperature is given by the equation  $R_t = [65.01 + 0.86t + 0.0029t^2] \times 10^5$  ohms. The constants depend on annealing and on the past history of the cell. Not more than 0.04 of the "light effect" is attributable to the heat produced by light. A change of colour accompanies the change in resistance on warming crystals of selenium produced by sublimation. The experiments suggest that if transformation into allotropic forms occurs, as seems probable, this takes place at all temperatures and the various modifications are in dynamic equilibrium, the quantity of each variety depending on the temperature. The degree of stability of each modification depends on the time during which it is maintained at one temperature.

J. R. P.

**Chemical Action of the Electric Discharge.** I. G. POMA (*Gazzetta*, 1921, **51**, ii, 58—70).—A critical résumé is given of the different views which have been expressed regarding the nature of

the mechanism of the chemical actions exerted by the electric discharge (cf. following abstracts).  
T. H. P.

**Chemical Action of the Electric Discharge. II.** G. POMA and G. BASSI (*Gazzetta*, 1921, **51**, ii, 71—79).—The vapours of a number of organic compounds have been subjected to the action of an intense explosive discharge from an induction coil, the resulting mixture of products being analysed. Compounds of low molecular weight lead to no separation of carbon, this commencing with compounds containing four atoms of carbon in the molecule and increasing with more complex compounds. Compounds with several oxygen atoms in the molecule form, in addition to carbon, water and various organic compounds, the latter in proportions too small to admit of analysis.

Methyl alcohol decomposes almost completely in accordance with the equation  $\text{CH}_3\cdot\text{OH}=\text{CO}+2\text{H}_2$ , only small proportions of carbon dioxide, acetylene, and methane being formed. With the higher alcohols, however, considerable quantities of acetylene and methane are obtained; the proportions of acetylene and carbon monoxide appear to depend solely on the molecular weight of the alcohol, whereas those of methane and hydrogen are influenced also by the molecular structure, the methane increasing with the proportion of methyl groups in the molecule.

Formic acid vapour gives approximately 1, 2, and 1 vols. of carbon dioxide, carbon monoxide, and hydrogen respectively, together with small amounts of acetylene and methane; the decomposition evidently occurs in two ways, represented by the equations,  $\text{H}\cdot\text{CO}_2\text{H}=\text{CO}_2+\text{H}_2$  and  $2\text{H}\cdot\text{CO}_2\text{H}=2\text{CO}+2\text{H}_2\text{O}$ . When, however, the molecular weight is increased, either by esterification of the formic acid or by passage to higher homologues, the proportion of the carbon dioxide formed diminishes considerably, but not regularly.  
T. H. P.

**Chemical Action of the Electric Discharge. III.** G. POMA and A. NESTI (*Gazzetta*, 1921, **51**, ii, 80—94).—By means of a Siemens ozoniser the action of the dark electric discharge on the vapours of a number of compounds has been investigated. With methyl alcohol, the mixture of gaseous products formed has the following percentage composition by volume: carbon monoxide, 10.8; methane, 15.5, and hydrogen, 73.3; formaldehyde is produced, but the other liquid and solid products of the reaction have not yet been investigated. The changes taking place are probably represented by the equations:  $\text{CH}_3\cdot\text{OH}=\text{CO}+2\text{H}_2$ ,  $2\text{CH}_3\cdot\text{OH}=2\text{CH}_4+\text{O}_2$ , and  $\text{CH}_3\cdot\text{OH}=\text{H}\cdot\text{CHO}+\text{H}_2$ ; the oxygen liberated probably unites with hydrogen to form water.

With ethyl alcohol, the gaseous products contain, in percentages: carbon dioxide, 2.2; carbon monoxide, 4.4; acetylene and ethylene, 9.0; methane and ethane, 26.0, and hydrogen, 59.0; acetaldehyde and other products are also formed. In the case of formic acid, the decomposition appears to take place according to the two equations,  $\text{H}\cdot\text{CO}_2\text{H}=\text{CO}_2+\text{H}_2$  and  $2\text{H}\cdot\text{CO}_2\text{H}=2\text{CO}+2\text{H}_2\text{O}$ , the gaseous products containing 22.4% of carbon dioxide, 53.6% of

carbon monoxide, and 23.8% of hydrogen; the liquid product distils completely. With acetic acid, the gaseous products have the percentage composition: carbon dioxide, 35.4; carbon monoxide, 18.5; methane and ethane, 17.3, and hydrogen, 28.3, and are apparently formed by the reactions,  $2\text{CH}_3\cdot\text{CO}_2\text{H} = 2\text{CO}_2 + \text{C}_2\text{H}_6 + \text{H}_2$  and  $\text{CH}_3\cdot\text{CO}_2\text{H} = \text{CH}_4 + \text{CO}_2$ ; the liquid product distils without residue. In the case of acetone vapour, the electrical conductivity is greater than with the above compounds, and less gaseous products are formed, the percentage composition of these being: carbon dioxide, 1.6; acetylene and ethylene, 5.0; carbon monoxide, 38.1, and methane and ethane, 55.3; hence for the gaseous phase the principal reaction is  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_3 = \text{CO} + \text{C}_2\text{H}_2$ . The liquid products contain a  $\gamma$ -diketone, probably acetonyl acetone. With methyl ethyl ketone vapour, the gaseous products have the percentage composition: acetylene and ethylene, 12.5; carbon monoxide, 32.8; methane and ethane, 43.6, and hydrogen, 10.2; the liquid products were shown to contain *s*-dimethylacetonyl acetone, but were not analysed completely.

In general, the dark electric discharge favours endothermic chemical reactions, although in some cases it may determine the sudden rupture of a false equilibrium, and hence cause an exothermic reaction. To a certain point parallelism exists between the action of the dark electric discharge and that produced by a rapid rise in temperature, although such parallelism is evidently imperfect.

T. H. P.

**Anodic Behaviour of Metals in Non-aqueous Solutions. II. Behaviour of Various Metals in Acetone Solutions.** UMBERTO SBORGI and PAOLO MARCHETTI (*Nuovo Cim.*, 1921, [vi], 22, 151-175).—The authors have investigated the anodic behaviour of various metals in acetone solutions of lithium chloride and silver nitrate, the apparatus and methods employed being identical with those used in the experiments on methyl alcoholic solutions (*Atti R. Inst. Veneto*, July, 1921).

In saturated solution of lithium chloride in acetone, anodes of nickel, cobalt, iron, zinc, and cadmium dissolve as bivalent metals and copper as a univalent metal, whilst aluminium dissolves to an extent greater than that calculated for a trivalent metal. The various phenomena accompanying the attack of the metal, such as formation of precipitates, coloration of the anodic liquid, etc., are discussed for each case. At the platinum cathode there takes place evolution of gas, deposition of lithium and lithio-acetone, and formation of precipitates containing the anode metal.

In saturated solutions of silver nitrate in acetone, anodes of iron, nickel, and cobalt exhibit passivity under various conditions and those of lead and aluminium show partial mechanical passivity, whilst copper is dissolved as a bivalent metal; the passifying influence of acetone is evident in all these cases.

These results and those obtained with nickel anodes in methyl alcoholic solutions (*loc. cit.*) show that metals that are passive and anions which are passifying in aqueous solutions exhibit the same

characteristics in non-aqueous solutions, although the solvent itself also exerts a decided influence.

T. H. P.

**Hydration of the Lithium Cation.** J. BARBOROVSKÝ and V. HANÁK (*Chem-Listy*, 1921, 15, 3—5).—The authors determined by a direct gravimetric method the increase in weight of the solution of lithium chloride at the cathode. The amounts of lithium chloride and water that were carried to the cathode were calculated from the difference between the initial and final concentrations of the cathode solution. These data yielded the transport number of the lithium ion and the amount of water associated with the lithium ion. Presupposing that the chloride ion has no affinity for water, it is indicated that eighteen molecular proportions of water are linked with the lithium ion. CHEMICAL ABSTRACTS.

**Application of the Law of Mass Action to Strong Electrolytes and the Derivation of the General Equation of the Ionisation Isotherm.** WILLIAM HUGHES (*Phil. Mag.*, 1921, [vi], 42, 428—431).—The equation previously deduced (this vol., ii, 481) is applied to obtain a general relation between  $V$  and  $\alpha$ , of which the equations of Ostwald, Rudolphi, van't Hoff, and Partington are special cases. Complete ionisation need not be assumed, and the law of mass action holds good in the case of strong electrolytes if active mass is represented by a momentum term, as is necessary in all applications of the law. The suggestion that the abnormality of strong electrolytes is due to the abnormal osmotic behaviour of the ions is in entire agreement with the fundamental assumptions made.

J. R. P.

**The Transformation of Iron at the Curie Point.** P. DEJEAN (*Compt. rend.*, 1921, 173, 412—414).—A comparison of the intensity of magnetisation of a cylindrical steel bar 1.2 m. long and 20 mm. in diameter with that of a similar bar composed of 120 small cylinders 10 mm. long and 20 mm. in diameter having varying definite interspaces between the small cylinders. The variation of the intensity of magnetisation with the interspace is of the same type as its variation with temperature. This is explicable if an increase in temperature provokes a progressive spreading of the elementary magnets in the bar. This may be produced by a progressive transformation of a magnetic  $\alpha$ -form, stable in the cold, into an isomorphous, non-magnetic  $\beta$ -form, stable at higher temperatures or simply by a spreading of the magnetic elements progressive with rise in temperature.

W. G.

**The Importance of Experiments at Very Low Temperatures.** C. A. CROMMELIN (*Chem. Weekblad*, 1921, 18, 483—487, 499—503, 515—519).—A discussion chiefly of the work of Kamerlingh Onnes and his co-workers at Leiden on critical point phenomena, and the relation between magnetic susceptibility and temperature.

S. I. L.

**Relationships of the van der Waals Constants.** W. HERZ (*Zeitsch. Elektrochem.*, 1921, 27, 373—375).—A theoretical paper in

which it is shown that van der Waals's constants,  $a$  and  $b$ , in the case of non-associated liquids, can be calculated from : the number of atoms in the molecule ( $n$ ), the number of valencies in the molecule ( $z$ ), from critical data, and other constants. In the case of the constant  $b$ , the value may be ascertained by the expressions (1)  $b=412n10^{-6}$ ; (2)  $b=201z10^{-6}$ ; (3)  $b=795.16M^210^{-4}/T_c^2d_s$ ; (4)  $b=12354d_s10^{-3}/p_k^2$ . The value of  $b$  as calculated by each of these expressions is recorded for twelve substances and the results are compared with the standard values. It is shown that there is an approximate agreement among the values, those obtained from formula 4 being the least in agreement. The constant  $a$  calculated from, (5)  $a=5.094nT_c10^{-6}$ ; (6)  $a=2.49z.T_c10^{-6}$ ; (7)  $a=4.5846n^2p_k10^{-6}$ ; (8)  $a=1474.713M^210^{-6}/T_c^2d_s$  and (9)  $a=239920d_sT_c10^{-6}/p_k^2$ . The value of  $a$  is calculated by all the above formula for eleven substances, and a fair general agreement with the accepted values obtained. A formula is developed whereby the coefficient of expansion of normal organic liquids may be calculated from the van der Waals constants. This has the form  $K_{20}=1\frac{1}{2}(a/0.00618b)-293$ . The agreement between the value of  $K_{20}$  calculated by the above formula and the experimental value is moderate. J. F. S.

**Nernst's Heat Theorem and Chemical Constant.** ЕИЧИ ЯМАЗАКИ (*J. Tokyo Chem. Soc.*, 1920, **41**, 19—35).—A mathematical paper, in which the explanations of the constant by Nernst and by Sackur are criticised. Calculated values, in good agreement with Nernst's values, are given for a number of substances.

CHEMICAL ABSTRACTS.

**Influence of Chemical Constitution on the Thermal Properties of Binary Mixtures. IV. The Constituents of Anthracene Oils.** PAUL PASCAL (*Bull. Soc. chim.*, 1921, (iv), **29**, 644—656; cf. A., 1913, ii, 292, 304, 1031).—The author has determined the melting-point curves of binary mixtures and some ternary mixtures of anthracene, phenanthrene, acridine, carbazole, retene, chrysene, and 4-methylacridine. Anthracene, phenanthrene, and carbazole, taken two by two or all three together, give a continuous series of mixed crystals. The melting-point curves of binary mixtures containing acridine as one component always show a minimum point. The introduction into a binary mixture of a constituent with an unsymmetrical molecule almost always results in isodimorphism, except in some cases when the lack of symmetry is due simply to the structure of side chains substituted in two symmetrical nuclei. W. G.

**Standardised Method for the Determination of Solidification Points, especially of Naphthalene and Paraffin.** R. M. WILHELM and J. L. FINKELSTEIN (*Bur. Standards, Sci. Papers*, 1919, **340**, 158—197).—The apparatus consists of a test-tube with thermometer and glass stirrer air-jacketed by insertion through the cork of a wide-mouthed bottle, which is immersed in a water-bath. The solidifying point corresponds with the first series of five or more readings, during which the temperature remains constant

( $\pm 0.02^\circ$ ). Usually under-cooling will occur, in which case the constant temperature should be observed immediately after the under-cooling ceases.

CHEMICAL ABSTRACTS.

**The Efficiency of certain Fractionating Columns in Distillation in a Vacuum. Some Laboratory Designs.** L. SMITH (*J. pr. Chem.*, 1921, 102, 295—304).—A preliminary account is given of the use of a large number of fractionating columns in the distillation of a mixture of glycerol monochlorohydrins under diminished pressure. The viscosity of the mixture inhibits the employment of all those types in which heads are used. It is found that the bulbous columns (including the Young "evaporator" still-head) have in general little efficiency and are markedly inferior to the "rod and disk" and Vigreux types. The reason of this is to be found in the incomplete mixing of the vapours in the more voluminous apparatus, a defect which must be more apparent in vacuum than in ordinary distillation, on account of the much greater velocity of the stream of vapour. The rate of distillation has an unexpectedly great effect on the separation; an efficient Vigreux column did not give any better result than the worst head when the rate of distillation with the former was two and a half times as great as with the latter. Efficient separation can only be obtained by distilling as slowly as possible, but, under these conditions, it is exceedingly difficult to keep the process uniform.

H. W.

**The Arrangement of the Molecular Volumes of the Oxides in the Periodic System.** D. BALAREFF (*J. pr. Chem.*, 1921, 102, 283—286).—A new table of molecular volumes of solid oxides is given. The graph showing the connexion between this factor and the atomic weights of the elements does not exhibit any striking regularity. The curves of the individual sub-groups are more uniform, eight of them having a minimum in the first portion.

H. W.

**Influence of Temperature on the Viscosity of Normal Liquids.** EDM. VAN AUBEL (*Compt. rend.*, 1921, 173, 384—387).—The variation of the viscosity of normal liquids with temperature may be represented by the equation  $\phi = m + n \log (\theta - t)$ , where  $\phi$  is the inverse of the viscosity,  $t$  is the temperature observed,  $\theta$  is the critical temperature of the liquid, and  $m$  and  $n$  are constants. This equation is verified in the cases of chlorobenzene, ethyl acetate, and benzene.

W. G.

**The Dimensions of the Molecules of Fatty Oils and some Phenomena of Molecular Solutions.** PAUL WOOG (*Compt. rend.*, 1921, 173, 387—390; cf. *ibid.*, 1921, 173, 303).—If a solid saturated fat and an unsaturated liquid fat in separate benzene solutions are poured successively on to water the products cover a surface equivalent to the sum of the areas of the molecules considered separately. They orientate freely on the water and do not influence one another. If, however, the two fats are dissolved together in benzene and the solution is poured on to water, the area covered

by the mixed molecules differs from the area calculated by addition. This phenomenon is attributed to an influence of the unsaturated molecules on the solid molecules. W. G.

**Behaviour of Cotton and Wool toward Substantive Dyes.** R. HALLER (*Kolloid Zeitsch.*, 1921, 29, 95—100).—It has been shown that diamine-blue-3R dyes vegetable fibre, as instanced by cotton, blue, whilst animal fibre is dyed corinth-red, as shown by wool. The behaviour of this dye has been investigated. It is shown that, as in the case of congo-rubin (this vol., ii, 28) solutions of diamine-blue-3R consist of particles of different degrees of dispersion. The highly disperse particles are corinth-red in colour, whilst the less dispersed particles are blue. These two types of particles may be readily separated by ultra-filtration. It is pointed out that generally cotton is dyed by the larger particles and wool by the more dispersed particles. This point is considered in connexion with the acid dyes and the benzidine dyes; the former are very highly dispersed whilst the latter consist of much larger particles, and it is the former class which dyes wool. It is pointed out that for each type of fibre (animal or vegetable) there is a definite specific degree of dispersion of the dye necessary for the maximum colour effect. In the cases of congo-rubin (*loc. cit.*) and diamine-blue-3R it has been shown that the degree of dispersion may be changed by the addition of neutral salts; hence it follows that by the use of a suitable concentration of a given neutral salt every substantive cotton dye is capable of becoming a usable wool dye. J. F. S.

**The Determination of Surface Tension from the Rise in Capillary Tubes.** SAMUEL SUGDEN (*T.*, 1921, 119, 1483—1492).

**Application of Dalton's Law to Concentrated Solutions.** RADU CERNATESCO (*Ann. sci. Univ. Jassy*, 1920, 10, 259—292; from *Chem. Zentr.*, 1921, iii, 199).—The freezing-point depressions of pairs of non-electrolytes were determined separately and when mixed for the same solvent. The osmotic pressure of the mixture may be less or greater than the sum of the osmotic partial pressures. The relation of the osmotic pressure to the sum of the partial pressures may also be reversed with increase or decrease of concentration. The Abegg formula is inadequate, and the facts can only be explained with the help of van der Waals's theory. A new formula for the osmotic pressure of mixtures, based on the modified Nernst formula of Bogdan (*Chem. Zentr.*, 1916, i, 1006) is devised. The anomalies observed in freezing-point depressions with strong electrolytes are probably due also to the fact that observed depressions are not equal to the separate partial depressions. G. W. R.

**Formation and Stability of Modifications of Polymorphous Substances Below their Transition Temperature.** O. MÜGGE (*Centr. Min.*, 1921, 504—505).—In reply to Brauns's criticism of the author's explanation of the genesis of doubly refracting boracite (this vol., ii, 387), it is pointed out that in the case of this mineral the transition from the highly symmetrical to the mimetic modi-

fection takes place with such rapidity that it is unlikely that growth could ever take place in the former modification at a low temperature. A temperature of 265° is assumed to have occurred only locally as a result of chemical processes.

E. H. R.

**Low Concentrations in Colloid Chemistry.** H. R. KRUYT (*Chem. Weekblad*, 1921, 18, 475—479).—A paper recapitulating the present knowledge of the influence of traces of electrolytes on the stability of colloidal sols.

S. I. L.

**Sulphide Sols. II. Sol Preparation by means of Gaseous Hydrogen Sulphide.** FRIEDRICH-VINCENZ VON HAHN (*Kolloid Zeitsch.*, 1921, 29, 139—143).—The author has investigated the production of metallic sulphide sols by the action of gaseous hydrogen sulphide on solutions of salts. The influence of temperature, rate of passage of the gas, and duration of the treatment on the stability of the resulting sol has been particularly considered. These three factors are shown to have a determining influence on the stability. The velocity of precipitation is known to have a considerable influence on the dispersion of the resulting system. The more rapid the formation the greater in general is the degree of dispersion. In the present case, the formation of the precipitate reaches its maximum velocity when the duration of treatment with the gas has reached a definite value; consequently further treatment is without any influence on the stability of the system. The same applies to the temperature; that is, there is a particular temperature at which the velocity of precipitation, the dispersion, and the stability of the sol produced are at a maximum and further increase of temperature is without influence. The velocity of precipitation increases also with the rate of passage of the gas. All three factors tend to increase the velocity of formation and thereby the degree of dispersion, which means an increase in the stability (cf. this vol., ii, 40).

J. F. S.

**Theory of Gels. III.** SAMUEL CLEMENT BRADFORD (*Biochem. J.*, 1921, 15, 553—562; cf. A., 1920, i, 452).—The reversible sol-gel transformation of the natural emulsoids is an extreme case of crystallisation and solution in conformity with von Weimarn's ideas. The true solubility of gelatin in water at 18° is 0.12 gram per 100 c.c. A 0.13% solution is metastable and has a blue opalescence. On slight increase of concentration, the gelatin is deposited as particles, mostly just below microscopic size. A further increase of concentration increases the bulk of the precipitate, the particles decrease in size, and at about 0.7% the precipitate fills the solution as a white, cloudy jelly. Similar results were obtained with agar, and small spherulites with starch. Clear gelatin gels become opalescent and develop spherulites on prolonged keeping.

G. B.

**General Colloidal Chemistry. II. Time Change of Colloidal Stannic Acid after Peptisation with Alkali Hydroxide Solution.** ADOLF STEGLER (*Kolloid Zeitsch.*, 1921, 29, 65—81).—The electrical conductivity and hydrogen-ion concentration of solutions of



stannic acid in potassium hydroxide of varying concentrations have been determined at 25° at various times over long periods. It is shown that colloidal stannic acid after peptisation with potassium hydroxide shows a change in its specific conductivity with time. With a series of solutions of stannic acid of different amounts of stannic acid in a solution of potassium hydroxide of constant composition, it is found that the solutions richer in tin undergo an immediate increase in specific conductivity, whilst the solutions poorer in tin at first suffer a decrease in conductivity followed by an increase. The increase in conductivity continues for months at a steadily decreasing rate. The concentration of hydroxyl ions decreases with time and is complete in about eight days. The specific conductivity of the colloidal portion has, in hydroxide solutions of all concentrations, a final value for the conductivity which is two to three times the initial value. The cause of the change in conductivity is considered, and shown not to be due to "temporary hydrolysis," as has been previously thought. The reactions represented by the equations (a)  $AB + HOH \rightleftharpoons AH + BOH$ ;  $mBOH + nAB \rightleftharpoons mBOH_nAB$ ; (b)  $AB + HOH \rightleftharpoons AH + BOH$ ;  $2BOH \rightarrow B_2O + H_2O$ , may be taken as representing the cause of the conductivity changes.

J. P. S.

**The Hydration of the Fibres of Soap Curd. I. The Degree of Hydration determined in Experiments on Sorption and Salting Out.** JAMES WILLIAM MCBAIN and HERBERT ERNEST MARTIN (T., 1921, 119, 1369—1374).

**The Hydration of the Fibres of Soap Curd. II. The Dew-point Method.** JAMES WILLIAM MCBAIN and CYRIL SEBASTIAN SALMON (T., 1921, 119, 1374—1383).

**Structures in Disperse Systems.** G. WEISSENBERGER (*Kolloid Zeitsch.*, 1921, 29, 113—124).—A theoretical paper in which the structure of disperse systems is considered on the basis of a large amount of work published by the author and others. It is shown that solutions of dispersoids, when a definite concentration is exceeded, possess a tendency whereby the particles assume an ordered arrangement. The cause of this is found in the interference with the free spatial movement of the particles. Consequently, the phenomenon is not observed in suspensions, since these have particles which, not being surrounded by a water sheath, are very small and their free movement is not interfered with until the concentration becomes very great. On the other hand, emulsoids and pseudo-emulsoids, which have particles surrounded by water sheaths and consequently may be very large, are systems in which the hindrance to free motion may be very great and is readily observed. Even at low concentrations, this occurs and furnishes the tendency to the structure formation. The elements of structure formation are the primary particles (micellæ); these may be either of a crystalline nature or a conglomeration of molecules. The arrangement of the molecules in these aggregates follows definite laws, since in similar circumstances

the same aggregates are always produced, but a change in the conditions brings about a change in the size and density of the aggregate. The primary particles are resistant and are the carriers of chemical reactions; they may preserve their size and other properties unchanged through a chemical reaction. In emulsoids and dispersoids, small discontinuities are often observed microscopically. These are not accidental, since the same type of discontinuity always occurs in identical circumstances. In addition to the primary structure elements, larger structure elements are also formed by the aggregation of numbers of primary elements. In such structure aggregates, the area of the particles actually touching becomes smaller in relation to the total mass the larger the number of primary structure elements composing the aggregate, and in consequence the solidity and resistance of the structure decreases very rapidly the larger the secondary structure elements. These colloidal structures are destroyed by chemical and mechanical forces in exactly the same way as crystalline structures, and are reformed in the same way. There is a concentration region where the formation of a colloidal structure is at its optimum, which is generally found in the region of small dispersion and in the neighbourhood of the turbidity conditions. By suitably choosing the concentration relationships, it is possible to follow the formation of the colloidal structure microscopically right up to the macroscopic structure.

J. F. S.

#### Colloid-Chemical Phenomena in the Tyrosinase Reaction.

HUGO HÄHN (Kolloid Zeitsch., 1921, 29, 125—130; cf. this vol., ii, 528).—The author has investigated the nature of the variously coloured melanin obtained in the tyrosinase reaction. In the ordinary course of the reaction, the melanin passes through a series of colours, red, brown, violet, blue, and black. It is shown that the ferment tyrosinase consists of two parts, the enzyme,  $\alpha$ -tyrosinase, and an inorganic salt. Neither the enzyme nor the inorganic salt alone will effect the reaction, but a mixture of the enzyme and an inorganic salt (calcium chloride, zinc sulphate, cadmium sulphate, and many others) effects the reaction, although not always is the scheme of colours passed through, but the black product is obtained in every case. A number of experiments tend to show that the essential difference between the red and black melanin is a difference in the degree of dispersion. This cannot be definitely proved until the constitution of melanin is established, but both substances undergo similar changes, for example, with hydrosulphite, and are thus shown at least to be similar. Both substances are negatively charged. The tyrosinase reaction is shown to be composed of two parts, (a) a biochemical, and (b) a colloid-chemical reaction. In the former, the  $\alpha$ -tyrosinase breaks up the tyrosine molecule and in the presence of the inorganic salt builds up the red melanin molecule. This is followed by the second reaction, in which coagulation changes the finely dispersed red phase into the coarsely dispersed black phase, after which precipitation occurs.

J. F. S.

**New Physico-chemical Law. The Law of Variability.** JOSEPH ERLICH (*Ann. Chim. Analyt.*, 1921, 3, 246—250).—A theoretical paper in which the variability of a system is discussed. It is shown that it is often not simple to fix the variability from considerations of the phase rule, this involving as it does the arbitrary quantity, "number of components." The present paper gives a method of fixing the variability of a system in all cases where the concentrations are only susceptible of change in relation to one and the same phase, the rest remaining invariable. It is shown that where gases constitute one of the phases of a system, the variability is equal to the number of gases, and in systems in solution where there is no gaseous phase, the variability is equal to the number of substances less one. J. F. S.

**Physico-chemical Study of the Double Decomposition,  $(\text{NH}_4)_2\text{B}_4\text{O}_7 + 2\text{NaCl} \rightleftharpoons \text{Na}_2\text{B}_4\text{O}_7 + 2\text{NH}_4\text{Cl}$ , for the Technical Preparation of Borax.** U. SBORGI and C. FRANCO (*Gazzetta*, 1921, 51, ii, 1—57).—The authors first discuss the theoretical considerations relating to systems containing reciprocal pairs of salts in solution and the methods of representing graphically their solubilities in water. The system corresponding with the equation  $(\text{NH}_4)_2\text{B}_4\text{O}_7 + 2\text{NaCl} \rightleftharpoons \text{Na}_2\text{B}_4\text{O}_7 + 2\text{NH}_4\text{Cl}$  has been investigated at 0°, 10°, and 25°, it being found that the pair stable in a temperature zone below 25° is the one containing borax; the data obtained are expressed in accordance with Jänecke's formula. The solubility diagrams exhibit two invariant points, at constant pressure and constant temperature, the solid phase consisting of (I)  $\text{NaCl} + \text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O} + \text{NH}_4\text{Cl}$ , or (II)  $(\text{NH}_4)_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O} + \text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O} + \text{NH}_4\text{Cl}$ ; with the first there corresponds a congruent, and with the second an incongruent solution, the so-called transformation interval lying in the temperature zone considered.

The yield of borax is calculated for each point of the solubility diagram, the highest yields corresponding with that portion of the curve joining points (I) and (II) (above) nearest to the latter.

T. H. P.

**Deduction of the Laws of Chemical Statics from the Theorem of Virtual Work.** R. ARIANO (*Gazzetta*, 1921, 51, ii, 95—108).—In this mathematical paper it is shown to be possible to enunciate, as a single principle, the theorem of virtual work, which serves as the starting-point for the exact treatment of all problems of equilibrium. The co-ordination of chemical and mechanical statics thus produced aids in the deduction, from the comparison between various phenomena, of the general laws governing a large number of natural phenomena. Various applications of the principle are developed.

T. H. P.

**Reaction in the Dark between Chlorine and Trichlorobromomethane.** ALEXANDRA VON RANKE (*Zeitsch. Elektrochem.*, 1921, 27, 365—367; cf. Noddack, this vol., ii, 568).—The reaction between chlorine and trichlorobromomethane has been examined at 100°. The reacting substances were sealed in bulbs in such a way

that the chlorine was entirely dissolved and no gas space left. Other experiments were carried out in which the chlorobromomethane was diluted with 3—255 volumes of carbon tetrachloride. The reactions were allowed to proceed until a definite brown tint was reached, when the amount of bromine set free was estimated spectrophotometrically. The velocity of the bromine separation decreases with the dilution. From this it follows that the primary reaction is not due to the chlorine atoms. The velocity constant for the reaction is given by the equation  $K_2 = [\text{Br}_2]/[\text{Cl}_2] \cdot [\text{CCl}_3\text{Br}] \cdot t$ , from which the course of the reaction is regarded as follows: (i)  $\text{Cl}_2 + \text{CCl}_3\text{Br} = \text{CCl}_4 + \text{Cl} + \text{Br}$ , (ii)  $\text{Cl} + \text{CCl}_3\text{Br} = \text{CCl}_4 + \text{Br}$ , (iii)  $\text{Br} + \text{Br} = \text{Br}_2$ .

J. F. S.

**The Rate of Hydrolysis of Ethyl Orthoformate.** ANTON SKRABAL and OTTO RINGER (*Monatsh.*, 1921, 42, 9—46).—The hydrolysis of ethyl orthoformate takes place in accordance with the two separable equations:  $\text{CH}(\text{OEt})_3 + \text{H}_2\text{O} \rightarrow \text{H}\cdot\text{CO}_2\text{Et} + 2\text{EtOH}$  and  $\text{H}\cdot\text{CO}_2\text{Et} + \text{H}_2\text{O} \rightarrow \text{H}\cdot\text{CO}_2\text{H} + \text{EtOH}$ . The second reaction is the ordinary ester hydrolysis; its already determined velocities in acid and alkaline medium have been measured again, and the values  $k_1=0.192$  and  $k_2=1080$  at  $25^\circ$  are confirmed. The first reaction is shown to proceed too slowly in alkaline solution to permit measurement, so that ethyl orthoformate is not noticeably hydrolysed by water alone or under the influence of hydroxyl ions. On the other hand, in strongly acid solution it proceeds with extreme rapidity. The formation of formic acid from the ortho-ester in solutions of mineral acids must therefore occur at a rate equal to that of the acid hydrolysis of ethyl formate; this is shown to be the case. The rapid reaction can be measured in the presence of a hydrogen buffer solution of primary and secondary phosphate, the course of the change being followed by measurement of the ethyl formate present after known intervals of time. The latter is only very slightly attacked under the experimental conditions adopted. It is thus possible to isolate the process of hydrolysis of ortho-ester to formic ester and to measure its rate in a medium of constant acidity. The results show that it is a reaction of the first order and that a proportionality exists between the velocity and the hydrogen-ion concentration. On the basis  $[\text{H}^+]=1$ , the velocity constant  $k=70,000$ , which is unusually high in comparison with other acid hydrolysis constants.

In connexion with his experimental results and the similar investigations of Verkade (*A.*, 1914, ii, 256; 1916, ii, 234, 607; 1918, ii, 103), the hydrolysis of the three types, ROR', AOR, AOA' (in which R=alkyl, A=acyl), is discussed and it is shown that ethyl orthoformate belongs to the ether type.

H. W.

**Hydrolysis of Ethyl Oxamate.** ANTON SKRABAL and GRETE MURRY (*Monatsh.*, 1921, 42, 47—62).—The methods used are similar to those adopted with oxalic esters (*A.*, 1917, ii, 250; 1919, ii, 144). The hydrolysis in alkaline solution is effected in the presence of disodium phosphate:  $\text{CO}_2\text{R}\cdot\text{CO}\cdot\text{NH}_2 + \text{Na}_2\text{HPO}_4 + \text{H}_2\text{O} = \text{CO}_2\text{Na}\cdot\text{CO}\cdot\text{NH}_2 + \text{NaH}_2\text{PO}_4 + \text{R}\cdot\text{OH}$ . The course of the change is

followed by titration of the unaffected disodium to monosodium phosphate by *N*/10-hydrochloric acid in the presence of methyl-orange. The velocity constant for  $[\text{OH}'] = 1$  at  $25^\circ$  is found to be 48,000 for the methyl and 22,000 for the ethyl ester. The hydrolysis is also measured in *N*/10-hydrochloric acid solution, and is followed by titration with *N*/10-ammonia solution in the presence of alizarine; for  $[\text{H}'] = 1$ , the velocity constants are calculated to be 0.0020 and 0.0015 for the methyl and ethyl esters respectively.

The communication concludes with a long theoretical discussion, based on the results obtained by the author with oxalic esters, of the influence of change in one group on the reactivity of the second group in the case of symmetrical di-esters. It is frequently observed that such alterations which do not affect the second group with regard to one particular type of action are also without influence in all other kinds of action.

H. W.

**Catalytic Actions at Solid Surfaces. VI. Surface Area and Specific Nature of a Catalyst: Two Independent Factors controlling the Resultant Activity.** E. F. ARMSTRONG and T. P. HILDITCH (*Proc. Roy. Soc.*, 1921, [A], 99, 490—495; cf. A., 1920, ii, 608).—The apparent volume of reduced nickel prepared in various circumstances has been determined and compared with the catalytic activity of the preparation. It is shown that nickel hydroxide reduced on kieselguhr gives a much larger volume than the same substance or the fused oxide reduced in the absence of kieselguhr, and that this product is very much more active than the nickel produced from the other sources. The rate of reduction of nickel oxide is also studied. The time-reduction curves show an inflexion point which depends on the physical state of the oxide and the temperature. The authors consider that the more rapid initial reduction represents the production of metallic nickel from the surface of the oxide particles, the slower subsequent rate corresponding with the reduction of a denser central core of oxide: such partly reduced oxide represents a supported catalyst as in the case of reduced nickel on kieselguhr, and its superior activity is to be attributed to the same cause as that of the kieselguhr-nickel oxide. The relation of the activity of a supported nickel catalyst to its reduced metal content has been ascertained in the case of the hydrogenation of cotton-seed oil at  $180^\circ$ . The results show that the variations in the catalytic power of reduced nickel are to be ascribed to the different surface areas of the free nickel exposed, and do not require for their interpretation the assumption of the presence of any catalyst (such as an oxide) other than metallic nickel. J. F. S.

**The Stability of Atoms.** (SIR) ERNEST RUTHERFORD (*Proc. Physical Soc.*, 1921, 33, 389—394).—A lecture delivered before the Physical Society of London on June 10, 1921. A. A. E.

**Constitution and Stability of Atom Nuclei.** WILLIAM D. HARKINS (*Phil. Mag.*, 1921, [vi], 42, 305—339).—Seven experimental correlations between the stability and composition of atomic nuclei are summarised. Three methods of classifying

isotopes are: (1) into four classes according as the number of electrons and protons in the nucleus is odd or even; (2) into isotopic numbers, varying from  $-1$  for hydrogen and the lower isotope of helium,  $0$  for the most abundant atomic species, up to  $54$  for uranium; (3) according to series relationships. The problem of nuclear stability in relation to the above is discussed. There is a marked periodicity in the variation of abundance, atomic stability, and a number of functions which express the composition of atomic nuclei. The most important relations which can be utilised in the prediction of isotopes are that the ratio of electrons to protons in the nucleus is never less than  $0.5$  for stable atoms, and the number of isotopes is in general considerably greater for elements of even than for elements of odd atomic number.

J. R. P.

**Atomic Dimensions.** MARIANO PIERUCCI (*Nuovo Cim.*, 1921, [vi], 22, 189—198).—The author considers the question whether the numbers calculated by Bragg (A., 1920, ii, 538) as the true radii of the atoms are multiples of one and the same length, which he terms the "elementary length" (A., 1920, ii, 300). Division of the atomic volume by the Avogadro number gives what may be termed briefly the "volume of the atom," and from this, together with the assumption that the atom is spherical and that at the absolute zero the packing is as close as possible, the value of the "elementary length" is calculated to lie between  $0.036$  and  $0.039$  Å. The available data are insufficient to decide the above question, but from the table given by Bragg (*loc. cit.*) it is evident that the calculated atomic radii group themselves round the atomic radii of the inert gases, and that the atomic radii for neon, argon, krypton, and xenon are related almost exactly as the numbers,  $4\Delta : 6\Delta : 7\Delta : 8\Delta$ ,  $\Delta$  having the value  $0.34$  Å.; the latter is almost exactly nine times the "elementary length."

For the four inert gases for which Bragg has calculated the atomic diameter,  $d_A$  (*loc. cit.*), the latter (in Å.) is related to the absolute melting point,  $T_f$ , in accordance with the simple expression,  $T_f = 79d_A - 81$ . Bragg does not give the value of the atomic diameter of helium, but taking its absolute melting point as  $0-2^\circ$  Abs., the expression just given leads to the value  $1.025-1.05$  Å. for such atomic diameter. Since  $3\Delta = 1.01$  Å., the conclusion seems justified that the atomic radii of helium, neon, argon, krypton, and xenon are related as  $3 : 4 : 6 : 7 : 8$ .

T. H. P.

**The Elements regarded as Compounds of the First Order.** S. H. C. BRIGGS (*Phil. Mag.*, 1921, [vi], 42, 448—456).—If the elements are regarded as compounds of the atomic kernels (that is, the residues when all the electrons in the outer shell are removed) and electrons, their reactions with each other are precisely analogous to the reactions between binary compounds; for example, (a)  $K^+E + Cl^+E_7 = K^+[Cl^+E_8]$  (where  $E$ =electron) and (b)  $2KCl + PtCl_4 = K_2[PtCl_6]$ . There is no essential difference between the forces holding together atoms in a compound and those holding the kernels and electrons in an atom. There are only two elements, *proton*

and electron. The atomic kernels are compound radicles of proton and electron, some of which combine with electron to give strongly polar substances like alkali metals and others non-polar substances such as neon (cf.  $\text{NH}_4 + \text{Cl} = \text{NH}_4\text{Cl}$  and  $\text{C}_6\text{H}_6 + \text{Cl} = \text{C}_6\text{H}_5\text{Cl}$ ). The chemical elements are true compounds of the first order, Werner's "compounds of the first order" are really of the second order, and substances such as potassium platinichloride of the third order. Co-ordination is involved in all valency phenomena. J. R. P.

**Encounters between Non-spherical Gaseous Molecules.** A. O. RANKINE (*Proc. Physical Soc.*, 1921, **33**, 362—376).—An extension of the author's previous work (this vol., ii, 489) on molecular dimensions and structure derived from the combined data of the kinetic theory of gases and of X-ray crystal measurements. In the present paper, non-spherical molecules built up of atoms of unequal sizes are considered; the paper considers all cases of diatomic molecules and special cases of polyatomic molecules.

J. F. S.

**Valency Theory of G. Lewis and the Asymmetry of the Water Molecule.** EUSTACE J. CUY (*Zeitsch. Elektrochem.*, 1921, **27**, 371—373).—A theoretical paper in which, on the basis of the views put forward by Lewis (*A.*, 1916, ii, 310) in connexion with the statical atom, the author has developed formulæ for the molecules of water, hydrogen sulphide, and ammonia. It is shown that in water the linking angle is approximately the same as that between carbon bonds. The distance between the oxygen nucleus and the hydrogen nuclei is the same in both cases, but is different from that between the two hydrogen nuclei. The well-defined dipolar character of water is expressed by the above, for two hydrogen atoms lie in one half of the tetrahedron and two electron pairs in the other half. The asymmetric nature of the water molecule is confirmed by the molecular heat,  $6R/2$ , whereas a symmetrical structure would demand  $5R/2$ . An asymmetric structure favours association more than a symmetrical structure. The cases of ammonia and hydrogen sulphide can be considered in the same way.

J. F. S.

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## Inorganic Chemistry.

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**Reversible Reactions of Hydrogen and Carbon Monoxide on the Metallic Oxides.** GEORGES CHAUDRON (*Ann. chim.*, 1921, [ix], **16**, 221—281).—A more detailed account of work already published (cf. *A.*, 1914, ii, 721; 1920, ii, 182, 379; this vol., ii, 178).

W. G.

**Iodine Monochloride.** E. FOURNEAU and E. DONARD (*Bull. Sci. Pharmacol.*, 1920, **27**, 561—566).—The addition of sodium

chloride stabilises solutions of iodine monochloride to the same degree as does hydrogen chloride; it does not inhibit the first phase of iodine trichloride decomposition which yields iodine monochloride. A method for the estimation of iodine monochloride, based on the facts that, unlike free iodine, the monochloride is scarcely soluble in chloroform, whereas it is very soluble in ethyl ether, and that it liberates iodine from potassium iodide, yields results of moderate accuracy.

CHEMICAL ABSTRACTS.

**Density, Refractivity Relationship and Dispersion of Gaseous Nitrogen at its Boiling Point.**

ERICH GEROLD (*Ann. Physik*, 1921, [iv], 65, 82—96).—The density of gaseous nitrogen at the boiling point has been determined by the displacement method. Six determinations are recorded at temperatures 77.68—77.77° Abs., and from the mean the value  $d_g = 0.0044973 \pm 17 \times 10^{-7}$  at 741.10 mm. and 77.75° Abs., is calculated. The refractive index of gaseous and liquid nitrogen at the boiling point has also been determined. In the case of the gas, the following values have been obtained at 752.32 mm. and 77.97° Abs.;  $\lambda = 643.9$ ,  $n = 1.0010779$ ,  $\lambda = 546.1$ ,  $n = 1.0010847$ ,  $\lambda = 435.8$ ,  $n = 1.0011007$ , whilst the liquid at 745.12 mm. and 77.12° Abs. gave the values  $\lambda = 656.3$ ,  $n = 1.19844$ ;  $\lambda = 579.1$ ,  $n = 1.19876$ ,  $\lambda = 546.1$ ,  $n = 1.19918$ ,  $\lambda = 435.8$ ,  $n = 1.20142$ ;  $\lambda = 404.7$ ,  $n = 1.20258$ . Wiener has replaced the figure 2 of the Lorenz-Lorentz formula by the symbol  $u$ , which he terms the form number. The value of  $u$  is exactly 2 for substances the molecules of which are exactly spherical, but is greater than 2 if the form diverges from the spherical. In the present case, the value of  $u$  has been calculated from the formula  $(n_L^2 - 1)/(n_L^2 + u)d_L = (n_g^2 - 1)/(n_g^2 + u)d_g$ , in which  $d_L$  and  $d_g$  are the densities of the liquid and gas at the boiling point and  $n_L$  and  $n_g$  the respective refractive indices, and the mean value  $u = 2.16 \pm 0.04$  obtained. This value indicates that the nitrogen molecule behaves as though it were nearly spherical, but since for red light  $u = 2.04$ , it behaves as though more nearly spherical than in the case of violet light, where  $u = 2.26$ . Consequently it follows that the electron which is active in the absorption of light of short wave-length has a greater orbit than that operative in the absorption of light of longer wave-length.

J. F. S.

**The Attack of Metals by Sulphuric-Nitric Acid Mixtures.**

PAUL PASCAL [with GARNIER and LABOURASSE] (*Bull. Soc. chim.*, 1921, [iv], 29, 701—709).—An examination of the action of mixtures of sulphuric and nitric acids varying in proportion and concentration on aluminium, steel, and lead, the results being expressed as loss in weight of the metal in grams per square metre in twenty-four hours, a large excess of the acid being used, and the temperature being maintained at 16—18° for the aluminium and steel and 19—21° for the lead. The addition of sulphuric acid to nitric acid facilitates the attack of aluminium. With nitric acid alone, the presence of ammonium nitrate slightly increases the attack of the metal. For all the varying proportions of sulphuric and nitric



acids, there is a concentration corresponding with between 10 and 20% of water at which the resistance of steel is a maximum.

W. G.

**Fusion of Carbon.** SIEGMAR MÜNCH (*Zeitsch. Elektrochem.*, 1921, 27, 367—368).—On strongly heating graphite rods by means of a powerful electric current, they are shown to soften and become plastic and eventually to melt. A graphite rod 50 mm.<sup>2</sup> in cross section and 5 cm. long, when subjected to a current of 800 amperes at 25 volts, melts and may be welded to a large graphite block which serves as a carrier for the current used. The plastic graphite may be bent or compressed so that its diameter is doubled. An apparatus is described by means of which large quantities of graphite may be melted. The cooled molten graphite has a metallic lustre. The literature dealing with previous attempts to melt carbon is considered. (See following abstract.) J. F. S.

[**Fusion of Carbon**]. EUGEN RYSCHKEWITSCH (*Zeitsch. Elektrochem.*, 1921, 27, 368—369; cf. preceding abstract).—A criticism of statements made by Münch in connexion with the author's experiments on the fusion of carbon. It is pointed out that the large current (800 amperes) found necessary by Münch to fuse carbon was probably due to the experiment being carried out in the open air, where the cooling was very great. This also accounts for the very few drops of molten carbon obtained, since graphite burns in air at 900°.

J. F. S.

**The Action of Alkaline Hydrogen Peroxide on Silver [Nitrate] Solution and the Behaviour of Silver towards Dilute Sulphuric Acid.** F. SALKOWSKI (*J. pr. Chem.*, 1921, 102, 194—208).—When silver nitrate solution is added gradually to a dilute solution of hydrogen peroxide containing a little potassium or sodium hydroxide, a black precipitate is formed initially which becomes greyer as more of the silver nitrate solution is added, and ultimately resembles elementary silver. Analysis, however, shows it to be a mixture of silver and silver oxide in which the proportion of the former increases with increasing quantities of hydrogen peroxide in the solution. Silver peroxide is not present. Analysis is effected by treating the product with boiling dilute sulphuric acid (100 grams of acid made up to a litre with water), which almost completely dissolves the oxide, but only attacks metallic silver to a very slight extent. (The reason of this slight solvent action could not be elucidated; it does not appear to depend on the presence of atmospheric oxygen, nor does sulphur dioxide seem to be liberated during the process.) The black colour of the precipitate is therefore due to the presence of a black modification of silver which can be prepared in a very stable condition by adding a solution of silver nitrate (3%, 10 c.c.) to a solution of dextrose (10%, 20 c.c.) and sodium hydroxide (d 1.16, 5 c.c.).

Silver peroxide may be detected in the following manner. A small portion of the substance is heated to boiling for a short time

with an aqueous solution of an aliphatic amino-acid, preferably glycine or alanine, which must not be used in too small quantity. The formation of a silver mirror indicates the presence of silver peroxide, whereas silver oxide does not show this reaction. Also, when silver peroxide is covered with nitric acid ( $d$  1.2) a dark brown solution is produced which becomes lighter and finally colourless when heated, but retains its colour for days at the laboratory temperature. The second test appears to be somewhat more sensitive than the first.

H. W.

**Decomposition of Ammonium Carbonate with Calcium Sulphate.** BERNHARD NEUMANN [with WALTER GELLENDIEN] (*Zeitsch. angew. Chem.*, 1921, **34**, 441—442, 445—447).—The author has investigated theoretically the reaction between ammonium carbonate and calcium sulphate. The latter substance forms two hydrates and exists in three anhydrous forms. Although there is uncertainty as to absolute solubilities, it is known that the dihydrate, gypsum, has a maximum solubility at about  $38^\circ$  and that the most soluble form is the semihydrate, for which the figure may reach 1%. The dihydrate has a negative heat of solution, the other forms have positive heats.

It is calculated that the yield of ammonium sulphate with 25*N*-ammonium carbonate solution should be 99.97%, the value rising slightly with increasing concentration. The yield at any temperature is calculated from the equation:

$$\log_e K_1/K_2 = 2.303 \log K_1/K_2 = -Q/R \cdot T_2 - T_1/T_1 - T_2$$

where  $Q$  is the heat of solution of calcium sulphate, that of the carbonate being negligible. It is shown that the influence of temperature on the reaction equilibrium is slight.

Experiments showed that in all cases conversion was almost complete in an hour, but complete equilibrium was only reached in from fifteen to twenty hours. The maximum yields obtained were: for the dihydrate 85%, for the semihydrate and gypsum heated at  $00-300^\circ$  92%, and for anhydrite 90%. In all cases the yields increased slightly with the concentration of the ammonium carbonate solution. The yield with the dihydrate increased with the temperature up to  $38^\circ$ , and then remained constant. Owing to the decomposition of ammonium carbonate at  $58^\circ$ , heating beyond this point is useless. Change of temperature had no appreciable effect on the reaction with ignited gypsum. The discrepancy between these results and the theoretical yields of more than 99% was explained by determining the solubility curve of calcium sulphate in ammonium sulphate solutions of different strengths; the existence of a double salt,  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot \text{H}_2\text{O}$ , was indicated. The suggestion that the reaction might be further complicated by an appreciable solubility of calcium carbonate in ammonium carbonate solution was investigated and disproved.

C. I.

**Decomposition of Calcium Sulphate by Ammonium Hydroxide.** BERNHARD NEUMANN [with GERTRUD KOTYGA] (*Zeitsch. angew. Chem.*, 1921, **34**, 457—459).—Equilibrium conditions in the reaction  $2\text{NH}_4\text{-OH} + \text{CaSO}_4 \rightleftharpoons (\text{NH}_4)_2\text{SO}_4 + \text{Ca(OH)}_2$

were investigated. If  $Lm_1\alpha$  and  $2Lm_1\beta$  are the concentrations of the ions  $[SO_4]$  and  $[OH]$ , the ratio of the molecular solubilities of the products  $[Ca]\cdot[SO_4]$  and  $[Ca]\cdot[OH]^2$  is  $Lm_1^2\alpha^2/4Lm_1^3\beta^2$ , which ratio,  $k$ , is found to be 3821 at  $18^\circ$ . If  $x$  and  $y$  are the molecular ionic concentrations and  $a$  is the normality of the ammonia solution  $x/y^2=k$  and  $2x+y=a$ ,  $k$  being known,  $y$  is determined in terms of  $a$  and the yield for any concentration of ammonia thus obtained. It varies from 6.6% with  $N/100$ -ammonium hydroxide to 88% with  $10N$ -solution. The variation with temperature may also be calculated; up to  $37^\circ$  the yield falls. The reaction was experimentally investigated by shaking two flasks, one containing gypsum and water and the other gypsum and ammonium hydroxide solution, and estimating the sulphate in solution in each from time to time. For  $N/10$ -ammonium hydroxide, the yield was 33%, in agreement with the calculation, but with increasing concentration it fell rapidly instead of rising, with  $N$ -solution being only 3%. The reaction is thus useless for practical purposes. The reverse reaction,  $(NH_4)_2SO_4 + Ca(OH)_2 = (NH_4)OH + CaSO_4$ , gave a 96% decomposition with  $5N$ -ammonium sulphate solution, falling to 53% with  $N/4$ -solution. The latter is again in agreement with calculation; the figures for stronger solutions are in excess of those to be expected. All these divergencies occurring in all solutions except the weakest, are due to the varying solubilities of calcium sulphate in ammonium sulphate solutions caused by the formation of the double salt. C. I.

**The System Potassium Sulphate-Glucinum Sulphate-Water at  $25^\circ$ .** HUBERT THOMAS STANLEY BRITTON and ARTHUR JOHN ALLMAND (T., 1921, 119, 1463—1470).

**Phosphorescent Zinc Sulphide.** RUDOLF TOMASCHEK (*Ann. Physik*, 1921, [iv], 65, 189—215).—A method is described whereby phosphorescent zinc sulphide may be prepared so that a product of uniform and reproducible properties for the examination of the phosphorescence of this substance is now for the first time obtained. Using this method, zinc sulphide containing respectively manganese and copper as phosphorogens has been prepared, and the properties and the phosphorescence bands of these substances have been examined. The bands have been compared with those previously obtained with ill-defined material. The phosphorescence phenomena of zinc sulphide containing respectively bismuth, lead, silver, uranium, nickel, and cobalt have been examined, and a number of new phosphorescence bands found and measured. The whole of the bands are considered and the series nature pointed out. J. F. S.

**Corrosion of certain Complex Brasses in Sea-water. I.** L. BELLADEN (*Gazzetta*, 1921, 51, ii, 144—159).—Of three samples of delta metal examined, that showing the greatest resistance to the corrosive action of sea-water contains the highest proportions of lead, manganese, and iron, as well as a small percentage of

nickel, which is lacking in the other two. [Cf. *J. Soc. Chem. Ind.*, 1921, 701A.] T. H. P.

**The Theory of Smelting. III. Equilibria between Pairs of Metals and Sulphur.** The System, Copper-Antimony-Sulphur. W. GUERTLER and KARL LEO MEISSNER (*Metal u. Erz*, 1921, 18, 410—415).—It is shown that sulphur cannot exist in equilibrium with copper antimonide and that a reaction occurs with the formation of cuprous sulphide.  $2\text{Cu}_3\text{Sb} + \text{S} = 2\text{Cu}_2\text{S} + \text{Cu}_3\text{S}$ ;  $\text{Cu}_2\text{S} + \text{S} = \text{Cu}_3\text{S}$ . Cuprous sulphide melted with either antimony or the antimonides yields stable mixtures, but no ternary compounds are formed. Copper and antimony trisulphides react according to the equations:  $12\text{Cu} + \text{Sb}_2\text{S}_3 = 3\text{Cu}_2\text{S} + 2\text{Cu}_3\text{Sb}$ ;  $10\text{Cu} + \text{Sb}_2\text{S}_3 = 3\text{Cu}_2\text{S} + 2\text{Cu}_3\text{Sb}$ ;  $6\text{Cu} + \text{Sb}_2\text{S}_3 = 3\text{Cu}_2\text{S} + 2\text{Sb}$ . The rectangle Cu—Sb— $\text{Sb}_2\text{S}_3$ — $\text{Cu}_3\text{S}$  is subdivided into six triangles by the five quasi-binary intersections,  $\text{Cu}_2\text{S}$ — $\text{Cu}_3\text{Sb}$ ;  $\text{Cu}_3\text{S}$ — $\text{Cu}_3\text{Sb}$ ;  $\text{Cu}_2\text{S}$ —Sb;  $\text{Cu}_3\text{SbS}_2$ —Sb; and  $\text{CuSbS}_2$ —Sb. Two independent mixture gaps occur in the system, which are probably dependent on similar gaps in the binary systems Cu— $\text{Cu}_2\text{S}$  and Sb— $\text{Sb}_2\text{S}_3$ . J. F. S.

**Electrolysis of Cerium Salts in Aqueous Solutions.** A. B. SCHMÖTZ (*Tidskrift Kem.*, 1920, 17, 213—215, 228—232).—The double chlorides of cerium and iron were electrolysed in an aqueous solution in presence of lactic acid, the rotating, dome-shaped, lead-plated platinum cathode being inverted over the anode chamber; the latter consisted of a glass tube with a helical row of openings, the platinum wire anode being wound round the tube through which the anode liquid was drained. The product consisted of a cerium-iron alloy containing 59.4 to 67% of cerium, and was probably free from oxides. CHEMICAL ABSTRACTS.

**Aluminium.** E. RATTENBURY HODGES (*Chem. News*, 1921, 123, 141).—Aluminium foil is unattacked by boiling strong acetic acid even after eighteen days in the absence of air; on exposure to the air for a week, traces of aluminium were found to have dissolved. If, however, a few drops of hydrogen peroxide are added to strong acetic acid in which a strip of the metal is immersed, the whole dissolves at 15° within thirty hours. Slightly warmed aluminium foil reacts with bromine with brilliant incandescence, the mixture evolving a heavy grey vapour of anhydrous bromide and leaving a brown, granular residue which soon deliquesces to a liquid from which colourless tabular crystals may be obtained on evaporation. Whilst citric and tartaric acids have no effect on the metal, oxalic acid dissolves it very slowly in the cold but more readily on heating, the solution, on evaporation, yielding an oily-looking colloidal film which deliquesces in moist air. Strong phosphoric acid readily dissolves aluminium foil, whereas it has no action on tin foil; this difference serves to distinguish between the two elements. A. R. P.

**Equilibrium Diagram of the System, Silicon-Iron.** TAKEJIRO MURAKAMI (*Sci. Rep. Tôhoku Imp. Univ.*, 1921, 10, 79—92).—Silicon-iron alloys containing up to 32.7% of silicon

have been prepared and subjected to magnetic, thermal, and micro-analysis and the equilibrium diagram has been constructed. It is shown that there are two compounds,  $\text{Fe}_3\text{Si}_2$  and  $\text{FeSi}$ , in the system. The former is magnetic with its critical point at  $90^\circ$ , whilst the latter is non-magnetic. An alloy corresponding with the formula  $\text{Fe}_2\text{Si}$  (20% Si) is neither a compound nor a saturated solid solution, as stated by Tammann and Guertler (A., 1906, ii, 32). The compound  $\text{Fe}_3\text{Si}_2$  dissolves in iron up to 16% of silicon at ordinary temperatures. The critical point of its solid solution in iron gradually decreases from  $790^\circ$  to  $450^\circ$ , as the silicon content increases from 0 to 16%. As the temperature rises, the solubility increases to 23% of silicon at  $1020^\circ$ . By heating to a temperature above  $1100^\circ$ , the compound  $\text{Fe}_3\text{Si}_2$  dissociates into iron and  $\text{FeSi}$ , and in alloys containing more than 23% of silicon,  $\text{FeSi}$  separates primarily on cooling the melt, and at  $1020^\circ$   $\text{Fe}_3\text{Si}_2$  is formed. Photomicrographs of sections of a large number of alloys are appended to the paper.

J. F. S.

### Mineralogical Chemistry.

**The Structure of Humic Acids and Coals.** J. MARCUSSEN (*Zeitsch. angew. Chem.*, 1921, 34, 437—438).—The author criticises the assumption of Fischer and Schrader (this vol., ii, 210) that natural humic acids are phenolic in character and contain no furan ring, basing their conclusions on the effects of oxidation under pressure. Lignin, natural humic acids, lignite, and coal yield benzenecarboxylic acids, whilst cellulose and artificial humic acids from carbohydrates yield furancarboxylic acids. Chardet (*Rev. gen. Chim. pure appl.*, 17, 214) has shown, however, that the dry distillation of natural humic acids yields both furan and furfuraldehyde in addition to phenolic compounds. Fischer and Schrader have recently (*Brennstoff-Chem.*, 1921, 2, 216) obtained furancarboxylic acids as well as benzenecarboxylic acids by the oxidation under pressure of artificial humic acids obtained by treating sugar with strong hydrochloric acid. If humic acids contain a *peri*-difuran ring (this vol., i, 313), this, on decomposition, would yield derivatives of either benzene or furan, according to the experimental conditions. Succindialdehyde is considered to be an intermediate product in the formation of humic acid from furan. An aldehyde acid (Humalsäure), closely related to humic acid, has been recently found in peat, but it is not found in lignite. The *peri*-difuran nucleus exists in coal and lignite, the presence of the bridged oxygen being proved, as with humic acid, by the behaviour with fuming sulphuric acid or with nitric acid, and the formation of double salts with iron chloride and with mercury bromide. The

author concludes that both cellulose and lignin have taken part in the formation of coal.

W. P.

### Analytical Chemistry.

**Micro-analysis of Gases by the Use of the Pirani Pressure Gauge.** RESEARCH STAFF OF THE GENERAL ELECTRIC CO., LTD. (N. R. CAMPBELL) (*Proc. Physical Soc.*, 1921, **33**, 287—296).—A method of analysis of small quantities of gases is described. The method consists in determining the condensation temperature of each gas consecutively. The gas contained in a side tube of a Pirani gauge is cooled to a temperature sufficient to liquefy the whole mixture, or, if some non-condensable gas is present, until the whole liquefiable portion has been liquefied. The temperature is then slowly raised and pressure-temperature readings are taken. A curve is produced which consists of a number of horizontal lines of constant pressure joined by a number of vertical, or nearly vertical, lines of constant temperature. The vertical temperature lines give the condensation temperatures of the individual constituents. The length of the ordinates serves as a relative measure of the quantity of each constituent. The total pressure admissible in the determination is 0.2 mm. and measurements may be made down to 0.001 mm. As cooling bath, the authors recommend freezing mercury ( $-39^{\circ}$ ), freezing chloroform ( $-65^{\circ}$ ), freezing acetone ( $-95^{\circ}$ ), freezing ethyl alcohol ( $-117^{\circ}$ ), and liquid air ( $-183^{\circ}$ ). In actual practice no thermometer is used, but the condensation temperatures of the mixture are compared with the condensation temperatures of the individual gases. To do this a number of gauges are made each containing one pure gas, and these are observed alongside the gauge containing the mixture. The method is very accurate and capable of wide application.

J. F. S.

**Losses in Chlorine in the Estimation of Chlorine in Organic Compounds by Incineration and their Prevention.** A. WEITZEL (*Arb. Reichs-Gesundh.-Amt*, 1920, **52**, 635—649; from *Chem. Zentr.*, 1921, iv, 228).—The ordinary methods for the estimation of chlorine in organic compounds by incineration are examined. The most suitable is the author's wet method (A., 1917, ii, 501). By observing certain precautions, however, chlorine can be estimated in the ash of organic compounds. Accurate results may be obtained if the substance is mixed with lime and water to form a cream, which is then dried and incinerated; or the substance may be incinerated after mixing with sodium carbonate and potassium nitrate.

G. W. R.

**The Estimation of Bromine in Salt Waters.** P. LEBEAU and M. PICON (*Bull. Soc. chim.*, 1921, [iv], **29**, 739—743).—A preliminary approximate estimation is made by titrating 1 c.c. of

the water with chlorine water containing 0.5 gram of chlorine per litre until decoloration just commences. The volume required represents approximately double the amount of chlorine required to displace all the bromine present as bromide.

A volume of water containing about 0.1 gram of bromine is placed in a separating funnel, 5 c.c. of 10% hydrochloric acid are added, and the calculated quantity of chlorine water containing 5 grams of chlorine per litre is run in. The liberated bromine is extracted with 15 c.c. of chloroform, and the chloroform extract is run into 10 c.c. of 10% potassium iodide solution in a stoppered bottle. The liquid in the separating funnel is again extracted with chloroform after the addition of 0.3—0.5 c.c. of chlorine water. This is repeated until the chloroform is colourless. The iodine liberated by the addition of the chloroform extracts to the potassium iodide is titrated with *N*/10-sodium thiosulphate. To obtain satisfactory results by this method the use of excess of chlorine water must be avoided, and the volume of water containing 0.1 gram of bromine as bromide should not exceed 25 c.c., a preliminary evaporation being conducted if necessary. W. G.

**Volumetric Estimation of Sulphurous Acid in Organic Substances by Distillation.** VICTOR FROBOESE (*Arb. Reichs-Gesundh.-Amt*, 1920, **52**, 657—669; from *Chem. Zentr.*, 1921, iv, 225).—The method proposed is a modification of that of Haase (A., 1882, 773). The sulphur dioxide obtained by distillation is collected in a standard solution of sodium hydrogen carbonate in the presence of hydrogen peroxide, whereby the sulphite is oxidised to sulphate. The excess of sodium hydrogen carbonate is titrated with hydrochloric acid, using methyl-orange as indicator. The sulphate formed may be estimated gravimetrically by precipitation with barium chloride as a control. The water used for the dilution of the liquid from which the sulphur dioxide is distilled must be free from oxygen. A long reflux condenser is desirable in order to prevent volatile organic acids from passing over. The method is applicable to the estimation of sulphites in cellulose-sulphite liquors, wine, dried fruit, and gelatin. G. W. R.

**Volumetric Method for the Estimation of Acids and Bases which yield Insoluble Salts.** G. BRUHNS (*Zeitsch. anal. Chem.*, 1921, **60**, 224—229).—A method described previously by Bucherer (A., 1920, ii, 702) yielded trustworthy results in the estimation of sulphates in crude sugars, molasses, etc.; the separation of the precipitated barium sulphate is facilitated by the addition of a small quantity of aluminium hydroxide, which, when kept for two days, becomes particularly insoluble in acid solutions. W. P. S.

**Modification of the Dumas Method, and Application of the Kjeldahl Method to the Estimation of Nitrogen in Nitro-naphthalenes.** PAUL H. M.-P. BRINTON, F. N. SCHERTZ, W. G. CROCKETT, and P. P. MERKEL (*J. Ind. Eng. Chem.*, 1921, **13**, 636—639).—In the modified Dumas method described, the carbon dioxide used is generated from dilute sulphuric acid and sodium

carbonate solution which are admitted to a large container filled originally with water; the gas is passed through two measuring bottles, one of which is filled with water, and the discharge of this from one bottle to the other, alternately, indicates the volume of carbon dioxide passing. The gas is then conducted, by a suitable arrangement of tubes and three-way taps, to the combustion tube, where the substance is burnt with copper oxide. The nitrogen is collected over sodium hydroxide solution, three nitrometers being used in connexion with each other; the combustion gases pass upwards through the first nitrometer, causing a circulation of sodium hydroxide solution from this to the others, and the liquid collecting in the levelling bulbs is returned to that of the first nitrometer as required. One of the nitrometers is provided with a water-jacket, and serves as the measuring vessel for the nitrogen.

To estimate nitrogen in nitronaphthalenes by the Kjeldahl method, about 0.5 gram of the substance is heated with 30 c.c. of sulphuric acid and 2 grams of salicylic acid for two hours on a water-bath, the mixture is then cooled, 2 grams of zinc dust are added, and after about eighteen hours the mixture is heated, first at 70°, and afterwards over a small burner, until all visible action ceases. One gram of mercuric oxide is next added, the mixture boiled for one hour, cooled, 7.5 grams of potassium sulphate are added, and the boiling is continued for a further period of one hour. The ammonia is then estimated by distillation in the usual way. The results obtained are lower than those found by the Dumas method, the difference increasing with the nitrogen content. For instance, 13.74% of nitrogen found by the Kjeldahl method corresponds with 14.33% by the Dumas method, and 15.48% with 16.85%.

W. P. S.

**Micro-estimation of Nitrogen and its Biological Applications.** M. POLONOVSKI and C. VALLÉE (*J. Pharm. Chim.*, 1921, [vii], 24, 129—134).—To estimate the total nitrogen, a portion of the substance containing from 1 to 2 mg. of nitrogen is heated for fifteen minutes in a test-tube with 1 c.c. of sulphuric acid and 1 gram of potassium sulphate. The mixture is then diluted with 6 c.c. of water, and the tube is connected with a small absorption vessel containing *N*/50-sulphuric acid; a current of air, heated previously by passing it through warm water containing a small quantity of sulphuric acid, is aspirated through the whole apparatus. After twenty minutes, the absorption apparatus is disconnected and the excess of sulphuric acid is titrated. Another portion of 3 c.c. of the original solution is then treated with 2 drops of acetic acid and a small quantity of sodium chloride, the mixture is heated at 90°, cooled, submitted to centrifugal action, and the nitrogen determined in an aliquot portion of the clear liquid; the difference between the two estimations gives the amount of nitrogen present as coagulable albumin.

W. P. S.

**Removal of Protein from Body Fluids for the Purpose of Simultaneous Estimation of Many Constituents.** GENKO MUKAI (*Biochem. J.*, 1921, 15, 516—520).—For the estimation of



non-protein nitrogen in serum, etc., the author boils the substance with sodium acetate and acetic acid, and removes the last traces of protein with talcum. The results are usually very slightly higher than those of the Folin-Denis method (A., 1912, ii, 703). G. B.

**Estimation of Sodium Nitrite.** F. MUHLERT (*Zeitsch. angew. Chem.*, 1921, 34, 448).—In the estimation of nitrites by the diazotisation method, *o*-aminobenzoic acid may be advantageously substituted for sulphanilic acid. The end point is sharp, the diazo-compound stable, and the reagent can be easily obtained in a pure state. C. I.

**Source of Error in the Estimation of Nitrate-Nitrogen by Ulsch's Method.** F. MACH and F. SINDLINGER (*Zeitsch. anal. Chem.*, 1921, 60, 235—238).—Traces of sulphide in the reduced iron used for the reduction of nitrates according to Ulsch's method cause the results obtained to be much too low. For instance, a potassium nitrate solution containing 13.86% of nitrogen yielded only 12.90% when the reduction was carried out with iron containing 0.03% of sulphur as sulphide. Each new quantity of reduced iron should, therefore, be tested against a pure nitrate before it is used for actual estimations. W. P. S.

**Estimation of Phosphorus in Iron, Steel, Ores, and Slags.** H. KINDER (*Zeitsch. anal. Chem.*, 1921, 60, 241—257).—A report of a critical examination of the molybdate method for the estimation of phosphorus, with particular reference to the influence of other elements. In the estimation of phosphoric acid in slags, the magnesium pyrophosphate method yielded results which were slightly higher (0.1 to 0.3%) than those yielded by the molybdate method. W. P. S.

**Double Arsenic Tubes.** GEORG LOCKEMANN (*Zeitsch. angew. Chem.*, 1921, 34, 396).—To economise in glass tubing, a piece of hard glass tubing is drawn out so that three portions of the original diameter of the tube are connected by capillaries, the whole being in one piece; the tube is used in conjunction with the ordinary Marsh apparatus. The first arsenic mirror is obtained in the first capillary; for the next estimation, the second wide portion and capillary are used, and the tube is then reversed and used in a similar manner for two further estimations. W. P. S.

**Micro-estimation of Carbon Monoxide in Blood.** MAURICE NICLOUX (*Bull. Soc. Chim. Biol.*, 1921, 3, 286—296).—A modification of the author's method (A., 1921, i, 204) for the estimation of carbon monoxide in blood is described; 2 to 5 c.c. of blood are used for an estimation, and it is claimed that the method is simple and accurate to within 2%. Notes are given on the application of the method to the estimation of the capacity of the blood for absorbing carbon monoxide, and of the amount of the latter present in blood in cases of poisoning. C. R. H.

**Estimation of Metals in Alloys of Known Qualitative Composition.** K. SCHMIDT (*Chem. Zeit.*, 1921, 45, 825—826).—From a knowledge of the atomic weights and specific gravities of the constituent metals of a binary or ternary alloy, together with the weight and volume of the alloy under examination, it is possible to calculate the percentage composition. The author has obtained formulæ for binary and ternary alloys involving in the first case the use of four constants based on the atomic weights and specific gravities of the constituent elements and these have been calculated for all the more important commercial binary alloys. [Cf. *J. Soc. Chem. Ind.*, 1921, Oct.] A. R. P.

**Estimation of Alkali Hydroxide and Carbonate in presence of Cyanide and Ferrocyanide.** F. MUHLERT (*Zeitsch. angew. Chem.*, 1921, 34, 447).—A method for the estimation of alkali in potassium or sodium cyanide consists in titrating the cyanide with silver solution, removing the turbidity formed at the end point with a drop of cyanide solution, and then titrating with normal acid until the turbidity reappears. The method is accurate if most of the alkali is present as hydroxide. In presence of other weak acids, for example, formic acid, this method cannot be used, neither does Clenell's method give good results. The best procedure is as follows. The cyanide is first titrated with silver solution, and the same quantity of solution added to another sample. The resulting solution after filtration can now be used for whatever alkalimetical estimations are desired. If great accuracy is not required, the solution need not be filtered. If ferrocyanide is present, the solution may be titrated directly with normal acid and methyl-orange. The cyanide having been previously estimated, the alkali is obtained by difference. C. I.

**Rapid Estimation of Silver in Alloys by a Modified Silver Chloride Method.** SAUERLAND (*Chem. Zeit.*, 1921, 45, 735—736).—About 0.5 gram of the alloy is treated with 10 c.c. of nitric acid, d 1.4, a small quantity of water is added, the mixture boiled, diluted to 80 c.c., again boiled, and, after five minutes, the insoluble matter (gold, tin, antimony) is collected on a filter and washed. A slight excess of hydrochloric acid is added, drop by drop, to the filtrate, the latter is then boiled, and the silver chloride is collected on a filter. The moist filter is then supported on the mouth of a small crucible, the upper part of the paper is wrapped round the end of a porcelain tube connected with a supply of coal gas, and the crucible is heated by a burner; the filter-paper chars, and after a time falls into the crucible, the silver chloride meanwhile being reduced by the coal-gas introduced through the porcelain tube. The reduction is completed by the incineration of the charred paper, and the resulting metallic silver is weighed. W. P. S.

**Simple Technique for the Estimation of Calcium and Magnesium in Small Amounts of Serum.** BENJAMIN KRAMER and FREDERICK F. TISDALL (*J. Biol. Chem.*, 1921, 47, 475—481).—One or 2 c.c. of serum, diluted with 2 c.c. of water, are mixed with

1 c.c. of saturated ammonium oxalate solution. The precipitate is collected by centrifuging and repeatedly washed in the same way with water and 2% ammonia, and is then titrated with  $N/100$ . potassium permanganate solution. An aliquot portion of the supernatant fluid of the calcium estimation is precipitated with ammonium phosphate; the ammonium magnesium phosphate is collected in a Gooch crucible and is dissolved in  $N/100$ -hydrochloric acid. Half the solution, mixed with 2 c.c. of a ferric thiocyanate solution, is compared colorimetrically with standards prepared with known amounts of ammonium magnesium phosphate. The error is  $\pm 5\%$  of the calcium and magnesium present. G. B.

#### Sensitiveness and Applicability of Qualitative Reactions.

**II. Barium Ions.** O. LUTZ (*Zeitsch. anal. Chem.*, 1921, 60, 209—223; cf. A., 1920, ii, 509).—The following are the minimum quantities of barium which can be detected by various reagents; in each case, 5 c.c. of the barium salt solution were treated with 0.5 c.c. of the reagent and the observation was made after five minutes. Sodium arsenate and ammonium chloride, 1:175; potassium ferrocyanide and ammonium chloride, 1:430; ammonium oxalate, 1:4400; sodium phosphate, 1:6200; aniline hydro-silicofluoride, 1:6000; ammonium carbonate and ammonia, 1:28000; sodium carbonate, 1:160000; sodium sulphite, 1:160000; ammonium chromate, 1:1200000; sulphuric acid, 1:1600000.

W. P. S.

**Application of Amalgams in Volumetric Analysis. I. Estimation of Molybdenum, Titanium, and Iron.** TAMAKI NAKAZONO (*J. Chem. Soc. Japan*, 1921, 42, 526—537).—About 0.15 gram of the metallic compound is reduced by vigorously shaking with 200 grams of liquid zinc amalgam and 10 c.c. of 2*N*-sulphuric acid during 0.5—1 minute in a specially made separating funnel, in which the air is replaced by carbon dioxide. After the reaction is completed, the solution is titrated with standard potassium permanganate solution. The method has been successfully applied to ammonium molybdate, titanous acid, and iron alum. The amalgam is prepared by heating 3 to 4 grams of zinc with 100 grams of mercury and some dilute sulphuric acid on a water-bath for one hour; the product is thoroughly washed with water and separated from solid residue. The amalgam may be used many times without loss of activity and the effect of some impurities in the metal on the accuracy is almost negligible.

K. K.

**Dimethylglyoxime Reactions of Iron and Cobalt.** WILH. VAUBEL (*Zeitsch. öffentl. Chem.*, 1921, 27, 163—164).—A deep red coloration is obtained when solutions of ferrous salts are treated with dimethylglyoxime solution and ammonia; the reaction is also given by ferric salts if a trace of ammonium sulphide is added before the ammonia. This coloration is distinct from that given by nickel salts, and there is no formation of a precipitate. Cobalt solutions give a yellowish-brown coloration with dimethylglyoxime

and ammonia; if ammonium sulphide is added before the ammonia, the coloration produced is bluish-violet to deep red.] W. P. S.

**Quantitative Separation of Tin and Antimony in the Presence of Phosphoric Acid.** (MLLE) MOURET and J. BARLOT (*Bull. Soc. chim.*, 1921, [iv], 29, 743—745).—The tin-antimony alloy is dissolved in aqua regia and the solution evaporated almost to dryness. The residue is taken up with warm concentrated hydrochloric acid and the solution diluted with an equal volume of water. To it is added at least 50 c.c. of an 8—9% solution of crystalline orthophosphoric acid for every 0.01 gram of tin present. The antimony is precipitated as sulphide by hydrogen sulphide at 80—90°, collected on a filter, and the antimony subsequently estimated electrolytically. The filtrate is boiled to remove hydrogen sulphide and the tin is precipitated by the addition of cupferron and estimated in the usual manner. W. G.

**Estimation of Titanium in Iron and Steel.** THEODOR DIECKMANN (*Zeitsch. anal. Chem.*, 1921, 60, 230—234).—One gram of the sample and 1 gram of iron free from vanadium are dissolved separately in dilute nitric acid, the two solutions are evaporated with the addition of sulphuric acid and heated until fumes of sulphuric acid are evolved; after cooling, the residues are boiled with dilute sulphuric acid, silica is separated by filtration, and the filtrates are treated with 10 c.c. of phosphoric acid ( $d$  1.3) and a few c.c. of hydrogen peroxide. Standard titanium sulphate solution is added to the solution containing the iron free from vanadium until the colour of this solution is brought to the same intensity as that of the solution containing the sample under examination. W. P. S.

**Estimation of Nickel and Copper on Nickel-plated or Copper-plated Iron Articles.** H. KOELSCH (*Zeitsch. anal. Chem.*, 1921, 60, 240—241).—The nickel or copper may be dissolved by immersing the metal in a hot sodium nitrite solution acidified with acetic acid; the iron does not dissolve as long as nitrite ions are present (see D.R.-P. 319855 and 330131). W. P. S.

**Estimation of Vanadium in Steels and Iron Alloys.** LUIGI ROLLA and MARIO NUTI (*Giorn. Chim. Ind. Appl.*, 1921, 3, 287).—Vanadium may be precipitated quantitatively from a solution containing about 1% of free hydrochloric or sulphuric acid by means of 4% aqueous "cupferron" solution in the cold, the precipitate being washed with 2% hydrochloric or sulphuric acid solution to which 2% of the 4% cupferron solution has been added, dried at about 70°, calcined and weighed as vanadium pentoxide. Iron and chromium may be easily separated from vanadium by precipitation by means of boiling sodium hydroxide solution. In the case of ferrovanadium, about 0.5 gram is treated with six times its weight of sodium peroxide in an iron crucible, the silica being removed after filtration and the iron as described above, and the

vanadium precipitated with cupferron. With steel, the hydrochloric acid solution is used, this being freed from silica and tungsten by filtration and from iron by treatment with ether; the liquid is boiled with sodium carbonate and filtered, the filtrate being treated with either lead acetate or lead nitrate and acetic acid. The lead vanadate thus precipitated is dissolved in dilute hydrochloric acid and evaporated with concentrated sulphuric acid. The residue is taken up in water and the vanadium precipitated in the filtrate by means of cupferron.

T. H. P.

**Denigès's Test for the Detection and Estimation of Methyl Alcohol in the Presence of Ethyl Alcohol.** ROBERT M. CHAPIN (*J. Ind. Eng. Chem.*, 1921, **13**, 543—545).—A modification of Denigès's method is described, the new procedure rendering the test more trustworthy. The alcohol is diluted until it contains 1% of total alcohols (solution A); 10 c.c. of this solution are mixed with 10 c.c. of 4% ethyl alcohol and diluted to 50 c.c. (solution B), and 10 c.c. of the latter solution are also mixed with 10 c.c. of 4% ethyl alcohol and diluted to 50 c.c. (solution C). Four c.c. of each of these solutions are placed in separate Nessler cylinders, and standards containing 1, 2, 3, etc., c.c. of 0.04% methyl alcohol solution, and 1 c.c. of 4% ethyl alcohol solution are prepared in other cylinders, the volumes in each case being diluted to 4 c.c. Each cylinder then receives the addition of 1 c.c. of phosphoric acid (1:5) solution and 2 c.c. of 3% potassium permanganate solution; after thirty minutes, 1 c.c. of 10% oxalic acid solution is added to each, followed, after two minutes, by 1 c.c. of concentrated sulphuric acid and 5 c.c. of Schiff-Elvove reagent. The colorations obtained are compared after the lapse of one hour. Acetone does not interfere with the method, but glycerol, carbohydrates, formic acid, acetic acid, and phenol, if present, should be removed by distilling the alcohol with the addition of sodium hydroxide; formaldehyde and terpenes are removed by treatment with silver nitrate and sodium hydroxide followed by distillation.

W. P. S.

**Possible Improvements in the Ebulliometric Estimation of Alcohol in Wines.** UGO PRATO LONGO (*Giorn. Chim. Ind. Appl.*, 1921, **3**, 290—293).—The construction of the scale, and the construction, control, and use of the ebulliometer, are discussed [see *J. Soc. Chem. Ind.*, 1921, 711A].

T. H. P.

**Application of the Determination of Miscibility Temperature to Alcoholimetry.** H. ROSSET (*Ann. Chim. Analyt.*, 1921, [ii], **3**, 235—239).—The miscibility temperature (the point at which the surface of separation of certain mixtures disappears) may be used to estimate the alcoholic strength of a liquid. For instance, when 5 c.c. of an alcoholic solution are mixed with 30 c.c. of pure acetone and 5 c.c. of standard light petroleum (b. p. 210—225°), the miscibility temperature varies from -5.5° for 90% alcohol to +27.6° for 65% alcohol. For lower alcoholic strengths,

a mixture of 50 c.c. of acetone and 5 c.c. of light petroleum is used, 5 c.c. of the alcoholic solution being added; in this case, the miscibility temperature varies from  $-1.0^{\circ}$  for 65% alcohol to  $+23.0^{\circ}$  for 28% alcohol.

W. P. S.

**Concentration and Purification of Alcoholic Fermentation Liquids. I. Distillation in Steam of certain Alcohols.**

JOSEPH REILLY and WILFRED J. HICKINBOTTOM (*Sci. Proc. Roy. Dublin Soc.*, 1921, **16**, 233—247).—The distillation constants of methyl, ethyl, propyl, *n*-butyl, *isobutyl* and *sec.*-butyl, and *isoamyl* alcohols have been investigated under experimental conditions similar to those employed in the recent work on fatty acids (A., 1919, ii, 528). Dilute solutions of the alcohols were distilled at constant volume, in most cases 200 c.c., water being introduced into the distillation flask at the same rate as distillation proceeded. The alcohol content of successive fractions of distillate was estimated from the density and by oxidation. The distillation constant,  $A=1/v \log a/a-x$ , in which  $a$  is the initial amount of alcohol in the flask and  $x$  the amount in the total distillate after a volume  $v$  has distilled, was found to increase with the molecular weight of the alcohols and to be greater for *sec.*- and *iso*-butyl alcohols than for *n*-butyl alcohol. For a given alcohol it was, as anticipated from general considerations, inversely proportional to the initial volume of liquid in the flask, and it also varied, although to a smaller extent, with the concentration of the alcohol, increasing as the concentration diminished. This variation of the constant with concentration confirms earlier work by Sorel (A., 1893, ii, 347) and Gröning. Several possible causes of these variations are discussed, and it is suggested that they may be accounted for by variations in the 'mass of water per c.c. of distillate.'

J. H. L.

**Estimation of Cresol by the Phenol Reagent of Folin and Denis.**

ROBERT M. CHAPIN (*J. Biol. Chem.*, 1921, **47**, 309—314).—Apart from other defects (cf., for example, Gortner and Holm, A., 1920, ii, 643), the estimation of phenols by the colorimetric method of Folin and Denis (A., 1915, ii, 802) suffers from the disadvantage that the phenol reagent gives colours of different intensity with equivalent quantities of different phenols. For the estimation of total cresol in mixtures of cresols of approximately known composition the author therefore introduces the use of empirical factors. The method is applied to the estimation of phenolic preservatives in serums.

E. S.

**Volumetric Estimation of Aminonaphthol-mono- and disulphonic Acids.**

GIORGIO RENATO LEVI (*Giorn. Chim. Ind. Appl.*, 1921, **3**, 297—302).—The aminonaphtholsulphonic acids may be titrated either with sodium nitrite in an acid solution or with diazo-compounds, comparison of the results obtained in these two ways serving as the best criterion of the purity of these compounds; the difference should be not more than 0.5% for a dry, or 0.2% for a pasty, product. The titration with nitrite is carried out by running  $N/5$ -sodium nitrite solution into a fresh solution or

suspension of the sulphonic acid containing free mineral acid; excess of the latter causes no appreciable increase in the velocity of diazotisation; the latter is, however, affected by the temperature, which should be to 10—12° at first and 25—30° at the end of the reaction. In the titration with diazo-compounds, the author makes use of either freshly-prepared diazobenzene or recently-titrated *p*-nitrodiazobenzene. In general, these aminonaphthol-sulphonic acids may undergo combination in two different ways, namely, in acid solution in the ortho-position to the amino-group, and in alkaline solution in the ortho-position to the hydroxyl group. Contrary to the statement made in many patent specifications, in acetic acid solution the combination occurs in the ortho-position with respect to the hydroxyl group. The colorations produced by the diazo-compounds of the aminonaphtholsulphonic acids are due to an internal combination, occurring either within a single molecule or between two molecules.

The aminonaphtholmonosulphonic acids examined were: M-acid ( $\text{NH}_2 : \text{OH} : \text{SO}_3\text{H} = 1 : 5 : 7$ ), S-acid ( $1 : 8 : 4$ ),  $\gamma$ -acid ( $2 : 8 : 6$ ), J-acid ( $2 : 5 : 7$ ) and R-acid ( $2 : 3 : 6$ ), and the disulphonic acids: 2S-acid ( $\text{NH}_2 : \text{OH} : \text{SO}_3\text{H} : \text{SO}_3\text{H} = 1 : 8 : 2 : 4$ ), H-acid ( $1 : 8 : 3 : 6$ ), K-acid ( $1 : 8 : 4 : 6$ ) and 2R-acid ( $2 : 8 : 3 : 6$ ). Taking the "nitrite number" as basis, the titration of the diazo-compounds may be effected as follows: M-, 2S-, and 2R-acids with *p*-nitrodiazobenzene in sodium carbonate solution, and J- and R-acids in acetic acid solution; S-,  $\gamma$ -, and K-acids in acetic acid solution, and H-acid in sodium carbonate solution, with diazobenzene. Qualitative characters for the differentiation between the various isomerides are given.

T. H. P.

#### The Estimation of Citronellol by the Formylation Method.

ALEXANDER ST. PFAU (*J. pr. Chem.*, 1921, **102**, 276—282).—The estimation of geraniol and citronellol by the formic acid method gives inexact results, in part because a portion of the geraniol undergoes esterification. Even with pure citronellol, however, the method gives uncertain data (cf. Schimmel & Co., A., 1914, i, 67; Simmons, A., 1916, ii, 117). The author's results are irregular and high when 100% acid is used, but low with a weaker acid. It is shown that the action of the acid on citronellol is not a simple process, fractionation of the product under diminished pressure leading to the isolation of citronellyl formate, b. p. 99—100°(corr.)/7 mm., the compound,  $\text{OH} \cdot \text{CMe}_2 \cdot [\text{CH}_2]_3 \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CHO}$ , b. p. 129°(corr.)/5 mm.,  $d_{20}^{25} 0.9651$ ,  $\alpha_D^{25} +1.46'$ ,  $n_D^{25} 1.4488$  and the corresponding *di-formate*,  $\text{CMe}_2 \cdot \text{O} \cdot \text{CHO} \cdot [\text{CH}_2]_3 \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CHO}$ , a colourless, highly refractive liquid, b. p. 140—141°(corr.)/7 mm., unchanged citronellol and, frequently, a small amount of more volatile liquid, possibly an aliphatic or a cyclic terpene. H. W.

**Estimation of the Composition of Ternary Mixtures: Ether-Water-Alcohol.** LOUIS DESVERGNES (*Mon. Sci.*, 1921, **11**, 145—150).—The composition of mixtures of ethyl ether, ethyl alcohol, and water is estimated by determining the quantity of water or of ether required to produce a turbidity, or the quantity

of alcohol required to produce a clear liquid when the mixture is not homogeneous; graphs are given which show the composition corresponding with the quantities of water, etc., added.

W. P. S.

**The Estimation of Sugar in Urine.** J. C. VAN DER HARST and C. H. KOERS (*Pharm. Weekblad*, 1921, **58**, 1230—1232).—The fermentation apparatus devised by Stephan under the name hydrosaccharometer has been found to be more trustworthy than Wagner's apparatus and to give results as accurate as those obtained by the polarimeter where the sugar content is not below about 1%. The Causse-Bonnans method has been re-examined, and again found unsatisfactory.

S. I. L.

**Volumetric Estimation of Phenylhydrazine and its Application to the Estimation of Pentosans and Pentoses.** ARTHUR ROBERT LING and DINSHAW RATTONJI NANJI (*Biochem. J.*, 1921, **15**, 466—468).—The carbohydrate is distilled in the usual way with 12% hydrochloric acid; an aliquot portion of the distillate is neutralised, slightly acidified, mixed with a standard aqueous phenylhydrazine solution (about 2%), kept at 50—55° for twenty minutes, and filtered; an aliquot part of the filtrate, containing excess of phenylhydrazine, is mixed with excess of standard iodine solution, and titrated with thiosulphate. The reaction is represented by the equation  $\text{PhNH}\cdot\text{NH}_2 + 2\text{I}_2 = 3\text{HI} + \text{C}_6\text{H}_5\text{I} + \text{N}_2$ . The results agree closely with those obtained by the phloroglucide method.

G. B.

**Identification of Ouabain and Strophanthin, and a New Test to Distinguish between the two Glucosides.** A. RICHAUD (*J. Pharm. Chim.*, 1921, **24**, 161—166).—To distinguish between ouabain and strophanthin in actual pharmaceutical practice where often only a milligram or so of the substances is available, the following differential characteristics may be utilised: Ouabain is soluble in 150 parts of water at 15°, whilst strophanthin dissolves in 40—43 parts at that temperature. The solution of the former is perfectly clear and colourless, and does not give a persistent froth on shaking. Strophanthin solutions, on the other hand, are inclined to be yellow, and are not perfectly transparent. They have a very pronounced bitter taste, and give a persistent froth on agitation. Under the microscope, ouabain appears as a pure white powder or small, rectangular tabular crystals, whilst strophanthin appears usually as a dirty or yellowish-white, amorphous powder, or crystallised in leaflets often grouped round a centre. Finally, a new colour reaction is proposed, which consists in warming in a water-bath at 60° or 70° in a test-tube 5 c.c. of concentrated hydrochloric acid, a few crystals of resorcinol, and a trace of the glucoside. Ouabain gives no coloration, and strophanthin a rose colour, the test depending, of course, on the difference in the sugars generated by the hydrolysis of the two glucosides.

G. F. M.

**Detection of Oxalic and Citric Acids.** M. POLONOVSKI (*J. Pharm. Chim.*, 1921, **24**, 167—168).—The usual method for the



detection of oxalic acid is simplified by the following procedure. The acid radicles are converted into sodium salts, and a saturated solution of calcium fluoride is added to the alkaline filtrate acidified with acetic acid. In presence of oxalic acid, calcium oxalate is precipitated under these conditions, its solubility in water at 15° being 0.00056%, whilst that of calcium fluoride is 0.05%. In the absence of fluorides from the original substance, a saturated solution of calcium sulphate may advantageously be substituted for the fluoride solution.

Citric acid may readily be detected in presence of any of the common organic acids by adding to the original solution potassium permanganate solution until the pink colour persists, then 1 c.c. of bromine water, and warming to decolorisation. In presence of citric acid, a precipitate of perbromoacetone is formed, but still more characteristic is the evolution of irritant vapours which attack the eyes, so that the least trace cannot possibly escape detection.  
G. F. M.

**Detection and Estimation of Lævulic Acid in Foods.** L. GRÜNHUT (*Z. Unters. Nahr. Genussm.*, 1921, **41**, 261—279).—Lævulic acid occurs in certain carbohydrate foods, and is usually accompanied by formic, acetic, and lactic acids; it may be identified by the red coloration which it yields with sodium nitroprusside in alkaline or acetic acid solution. A method for the estimation of lævulic acid depends on its oxidation to acetic acid by means of potassium dichromate and sulphuric acid; the resulting acetic acid is distilled and titrated. Formic acid under the same conditions is oxidised to carbon dioxide; if the amount of acetic acid found in the distillate is in excess of that calculated from the quantity of dichromate reduced (after allowing for the formic acid as estimated separately by the mercuric chloride method), the presence of free acetic acid in the sample is indicated. Lactic acid is also oxidised by dichromate to acetic acid. In the case of a sample containing all the four acids mentioned, the procedure adopted is to acidify the substance with phosphoric acid, extract the organic acids with ether (a quantity of sodium hydroxide is placed in the extraction flask to prevent volatilisation of the formic acid with the ether), then extract the ethereal solution with dilute sodium hydroxide solution and evaporate the united aqueous extracts to dryness. The dry residue is dissolved in a definite volume of water, the organic acids are liberated, and the solution is submitted to a simple distillation. The distillate contains the whole of the acetic acid, the greater part of the formic acid, a small quantity of lævulic acid and no lactic acid; the residual solution in the flask will contain the greater part of the lævulic acid, the remainder of the formic acid, the whole of the lactic acid, and no acetic acid. The two solutions are analysed separately as described.  
W. P. S.

**Detection and Estimation of Salicylic Acid in Wine.** W. FRESSENIUS and L. GRÜNHÜT (*Zeitsch. anal. Chem.*, 1921, **60**, 257—266).—Fifty c.c. of the wine are acidified with sulphuric acid,

extracted with a mixture of ether and light petroleum, the extract is evaporated, and the residue tested with ferric chloride. To estimate the salicylic acid, 500 c.c. of the wine are boiled under a reflux apparatus for one hour with the addition of sodium hydroxide solution, the mixture is then cooled, acidified with sulphuric acid, and extracted with ether-light petroleum mixture. The ethereal solution is evaporated with the addition of a small quantity of water, the residual aqueous solution diluted to a definite volume, and used for the colorimetric estimation of the acid by the ferric chloride method.

W. P. S.

**Estimation of Salicylates and Phenol.** W. O. EMERY (*J. Ind. Eng. Chem.*, 1921, **13**, 538—539).—A method for the estimation of phenol and salicylates, particularly salol (phenyl salicylate), depends on the formation of a red, amorphous compound, di-iodophenylene oxide, when phenol or salicylic acid is treated with iodine in the presence of sodium carbonate:  $2\text{PhOH} + 6\text{I}_2 + 4\text{Na}_2\text{CO}_3 = 2\text{C}_6\text{H}_4\text{OI}_2 + 8\text{NaI} + 4\text{CO}_2 + 4\text{H}_2\text{O}$ , and  $2\text{C}_6\text{H}_4(\text{OH})\cdot\text{CO}_2\text{H} + 6\text{I}_2 + 4\text{Na}_2\text{CO}_3 = 2\text{C}_6\text{H}_4\text{OI}_2 + 8\text{NaI} + 6\text{CO}_2 + 4\text{H}_2\text{O}$ . To estimate salol in admixture with acetanilide, phenacetin, and caffeine, a portion of the sample containing about 0.1 gram of salol is extracted with chloroform, the chloroform solution is evaporated, and the residue obtained treated with 10 c.c. of 1% sodium hydroxide solution and heated in a reflux apparatus at such a rate that it boils in two minutes; three successive quantities of 10 c.c., 30 c.c., and 50 c.c. respectively of water are then added, the mixture being boiled after each addition. One gram of sodium carbonate is added with the last quantity of water. An excess (35 to 60 c.c.) of *N*/5-iodine is then added to the boiling solution, the flask is removed from the condenser, a further 1 gram of sodium carbonate is introduced, and the mixture boiled gently for about twenty minutes. If phenacetin is present, the quantity of iodine solution mentioned should be increased by 5 c.c. for each 0.1 gram of phenacetin supposed to be in the mixture. The precipitate formed is collected, washed with 200 c.c. of hot water, dried at 100°, and weighed; the weight found is multiplied by 0.3113 to obtain the corresponding quantity of salol.

W. P. S.

**Estimation of the Saponification Number, Iodine-Bromine Number and Bromine-substitution Number [of Fats and Waxes].** E. SCHULEK (*Pharm. Zentr.-h.*, 1921, **62**, 391—395).—The use of propyl alcohol, as proposed by Winkler (A., 1911, ii, 550) is recommended in the estimation of the saponification number, since by the use of this solvent even waxes are saponified completely in a short time. In the case of the iodine-bromine number, the results obtained are the higher the longer the time of contact of the fat or oil with the reagent, particularly in the case of linseed oil, croton oil, and lanolin. The reaction in the estimation of the bromine-substitution number is practically complete after two hours' contact.

W. P. S.

**Colour Reactions of some Nitro-substances.** O. RUDOLPH (*Zeitsch. anal. Chem.*, 1921, 60, 239—240).—The following colorations are obtained when about 1 milligram of the substance is dissolved in 10 c.c. of alcohol or acetone and then treated with 2 c.c. of dilute sodium hydroxide solution or ammonia :

	Alcohol solution.		Acetone solution.	
	With sodium hydroxide.	With ammonia.	With sodium hydroxide.	With ammonia.
<i>o</i> -Dinitrobenzoic acid .....	colourless	colourless	colourless	colourless
<i>m</i> -Dinitrobenzoic acid .....	"	"	intense reddish-violet	pink to purple
<i>p</i> -Dinitrobenzoic acid .....	"	no characteristic colour	intense yellow	yellow
1:3:5-Trinitrobenzene ...	yellowish-red	yellowish-red	blood-red	blood-red
2:4-Dinitrotoluene .....	deep blue	colourless	deep blue	colourless
2:6-Dinitrotoluene .....	colourless	"	faint pink	"
2:4:6-Trinitrotoluene ...	deep yellowish-red	bright red	purplish-red	light red
1:3-Dinitronaphthalene ...	yellowish-red	red	yellowish-red	red

W. P. S.

**Assay of Aconitine.** A. R. L. DOHME (*Amer. J. Pharm.*, 1921, 93, 426—429).—A physiological method is described and recommended for the valuation of aconite and its preparations, since the ordinary chemical method of extracting the total alkaloids does not differentiate between the amount of aconitine, benzoyleconine, and aconine present, and there appears to be no method available for their separation. Aconitine is about three hundred times as toxic as benzoyleconine and four thousand times as toxic as aconine. In the case of the fluid extract, 1 c.c. is diluted to 10 c.c. with 50% alcohol, and small quantities of this solution, diluted to a volume of 1.5 c.c. with normal saline solution are injected into the subcutaneous tissues of the abdomens of guinea-pigs of about 350 grams body weight. The lethal dose is taken to be the smallest quantity which will kill within twenty-four hours. Approximately 0.0000005 gram per gram of guinea-pig is the lethal dose of aconitine.

W. P. S.

**Colorimetric Estimation of Carnosine.** WINIFRED MARY CLIFFORD (*Biochem. J.*, 1921, 15, 400—407).—A modification of Koessler and Hanke's colorimetric method for estimating iminazole derivatives (*A.*, 1920, ii, 67). The minced tissue is extracted with a known volume of water at 60—90°. The aqueous extract is then treated with metaphosphoric acid and filtered. An aliquot portion of the filtrate is neutralised to litmus and the depth of colour produced on admixture with sodium carbonate and *p*-diazobenzenesulphonic acid determined colorimetrically in a Duboseq colorimeter. Parallel estimations agree to 0.05 mm.

S. S. Z.

**Estimation of Acetanilide.** A. RECLAIRE (*Perf. Ess. Oil Rec.*, 1921, 12, 280).—A method, sufficiently accurate for technical purposes, for the estimation of acetanilide, particularly for acetanilide used as an adulterant in artificial musk preparations, is carried

out as follows: About 1.5 grams of the substance are boiled in an acetylation flask with 50 c.c. of 20% hydrochloric acid for fifteen minutes. The volume is then made up to 500 c.c., and to 25 c.c. an excess of a standard potassium bromide-bromate solution and 5 c.c. of strong hydrochloric acid are added. Tribromoaniline is precipitated and the excess of bromine estimated by potassium iodide and sodium thiosulphate in the usual way. One c.c. of  $N/10$ -thiosulphate equals 0.00225 gram of acetanilide. G. F. M.

**A Colour Reaction for Carbamide.** VICTOR ARREGUINE and EDUARDO D. GARCÍA (*Anal. Asoc. Quím. Argentina*, 1921, 9, 183—191).—The colour reactions for carbamide are discussed. The reaction proposed by the authors consists in adding resorcinol and hydrochloric acid to an aqueous solution of the substance under examination and boiling for about one minute. After cooling and dilution with water, the liquid is shaken with ether. The ethereal layer is coloured pink to red, according to the amount of carbamide present. Further colour changes in the ethereal layer are observed on addition of ammonia solution. One milligram of carbamide may be detected by this test, which is also given to a less degree by guanidine and substances giving carbamide under the conditions of experiment. The reaction would appear to be characteristic for the group  $=C(NH_2)_2$ . It is not applicable to the quantitative estimation of carbamide. G. W. R.

**Gasometric Estimation of Urea in Urine.** RAYMOND L. SEHLE (*J. Biol. Chem.*, 1921, 47, 13—17).—The hypobromite method gives results which agree with those obtained by the urease method (A., 1914, ii, 822) if the estimation is carried out in a vacuum after the removal of ammonium salts by means of permutite (cf. Youngburg, this vol., ii, 358). E. S.

**Estimation of Urea, Ammonia, and Amino-acids in Urine after Precipitation of the Ammonia.** PHILBERT (*J. Pharm. Chim.*, 1921, [vii], 24, 49—58. See also A., 1919, ii, 374).—Ammonia is precipitated as ammonium magnesium phosphate and separated by filtration; the filtrate is then treated with basic lead acetate, again filtered, and the urea estimated by the hypobromite method. Another portion of the urine, after the ammonia has been removed, is neutralised towards phenolphthalein, formaldehyde solution is added, and the mixture titrated with standard alkali solution. The results obtained are expressed in terms of nitrogen or of ammonia. W. P. S.

**Estimation of Dicyanodiamide and Urea in Fertilisers.** ERLING JOHNSON (*J. Ind. Eng. Chem.*, 1921, 13, 533—535).—A volumetric method proposed for the estimation of dicyanodiamide depends on the formation of the complex silver pierate dicyanoguanidine. Five grams of the sample are shaken for three hours with 450 c.c. of water and 5 c.c. of acetic acid, the mixture is then diluted to 500 c.c., filtered, and 100 c.c. of the filtrate are treated

with 5 c.c. of 20% nitric acid and 20 c.c. of sodium picrate solution (7.5 grams of picric acid neutralised with sodium carbonate and diluted to 100 c.c.; this solution is used at 40° to prevent crystallisation of the salt). The mixture is then cooled in ice-water and a slight excess of silver nitrate solution (7.582 grams per litre) is added and, after fifteen minutes, the whole is diluted to 200 c.c. and filtered. Five c.c. of 20% nitric acid and 2 c.c. of 5% ferric sulphate solution are added to 100 c.c. of the filtrate and the excess of silver is titrated with standardised thiocyanate solution. Each 1 c.c. of the silver nitrate solution is equivalent to 1% of diguanodiamide-nitrogen. The estimation of urea is based on the formation of urea oxalate; 5 grams of the sample are shaken with 100 c.c. of amyl alcohol, the solution is filtered, 50 c.c. of the filtrate are mixed with an equal volume of ether, and the urea is precipitated by the addition of 25 c.c. of a 10% solution of anhydrous oxalic acid in amyl alcohol. After thirty minutes, the precipitate is collected on a filter, washed twice with a mixture of equal volumes of amyl alcohol and ether, once with ether alone, dried under reduced pressure, and weighed. The precipitate contains 57.01% of urea.

W. P. S.

**Reaction for the Micro-chemical Detection of "Chinosol" or 8-Hydroxyquinoline Salts.** C. GRIEBEL (*Pharm. Zentr.h.*, 1921, 62, 452—456).—A 2% solution of "chinosol" (8-hydroxyquinoline sulphate), when treated with a drop of potassium ferrocyanide solution, yields a bright green, crystalline precipitate, the colour changing within a few minutes to orange-red. The precipitate is formed more slowly from dilute solutions, and is not given when the concentration of the solution is less than 0.5%. With potassium ferricyanide, 8-hydroxyquinoline sulphate solution yields a yellow, crystalline precipitate.

W. P. S.

**Estimation of Pyramidone (4-Dimethylamino-1-phenyl-2:3-dimethyl-5-pyrazolone) in Presence of Antipyrine (1-Phenyl-2:3-dimethyl-5-pyrazolone) and Aspirin (o-Acetoxybenzoic Acid).** E. OLIVERI-MANDALÀ and E. CALDERARO (*Gazzetta*, 1921, 51, i, 324—328).—Pyramidone may be estimated in presence of antipyrine and aspirin by taking advantage of the fact that the former, but not the latter, yields dimethylamine when boiled with concentrated potassium hydroxide solution (1:1); the amine is collected in a known volume of standard acid and its amount determined by titration: 1 gram of pyramidone is found to correspond with 8.50 c.c. of seminormal sulphuric acid, the theoretical number being 8.64 c.c.

\* When titrated with seminormal hydrochloric acid in presence of methyl-orange, 2 grams of pyramidone correspond with 16 c.c. of the acid and 0.9 gram of aspirin with 1 c.c. of the acid. Hence, the percentage (A) of aspirin in a mixture of the two compounds is given by the formula  $A = 9(16.6 - x)$ , where  $x$  denotes the number of c.c. of the seminormal acid required to neutralise 2 grams of the

mixture; then 100—A gives the percentage of pyramidone. [See, further, *J. Soc. Chem. Ind.*, 1921, 600A.] T. H. P.

**Estimation of Veronal in Urine and Human Organs.** L. VAN ITALIE and A. J. STEENHAUER (*Pharm. Weekblad*, 1921, 58, 1062—1068).—Ethyl acetate is preferable to ethyl ether for extracting veronal from urine, the solubility being 1:8.9 in the former, and 1:18.7 in the latter. When the extract is purified with charcoal, low yields are obtained owing to adsorption. Treatment of the urine with lead acetate or basic lead acetate effects precipitation of some of its constituents and prevents emulsification during the extraction; by treatment of the extract with potassium permanganate, a quantitative yield of pure veronal is obtained. The method is as follows: 100 c.c. of urine are treated with 10 c.c. of lead acetate (or basic lead acetate) solution, and filtered. The filtrate is evaporated to 25 c.c. and acidified with acetic acid. It is then extracted with twice its volume of ethyl acetate, filtered, and evaporated; the residue is dissolved in 10 c.c. of boiling water, with addition of 5 c.c. of dilute sulphuric acid, and  $N/10$ -potassium permanganate solution added until the supernatant liquid is colourless. The manganese oxide formed is decomposed with a few drops of hydrogen peroxide, the liquid is shaken with twice its volume of ethyl acetate, filtered, evaporated, and the residue dried at 100°. With suitable modification this method is applicable also to the estimation of veronal in various organs. W. J. W.

**The Colorimetric Estimation of Tyrosine and the Phenolic Number of Proteins.** PIERRE THOMAS (*Bull. Soc. Chim. Biol.*, 1921, 3, 197—216).—In the estimation of tyrosine in proteins by the colorimetric method of Folin and Denis (*A.*, 1912, ii, 1012) the presence of tryptophan, scatole, indole, and reducing reagents vitiates the results; hence the method is untrustworthy and must be rejected (compare Abderhalden and Fuchs, *A.*, 1913, i, 409; Folin and Denis, *A.*, 1913, i, 915). The author suggests the characterisation of proteins by means of their phenolic numbers, the latter being defined as the numbers, calculated in percentages of tyrosine, which represent the phenolic constituents of the hydrolysates. For the estimation of the phenolic number a weighed portion of the protein is hydrolysed with 25% sulphuric acid, filtered from humin, neutralised with barium hydroxide, acidified with picric acid, and filtered. Just sufficient mercuric nitrate is then added to an aliquot part of the filtrate to precipitate the tryptophan. After decolorisation, if necessary, by addition of a small quantity of animal charcoal, the colour produced by the addition of 2 c.c. of Millon's reagent to 10 c.c. of the filtered solution is compared with a tyrosine standard. The results of a number of estimations are given. E. S.

**Some Corollaries of the Laws of Hydrolysis by Enzymes.** H. COLIN (*Bull. Soc. Chim. Biol.*, 1921, 3, 263—272).—Deductions are made from the laws which govern hydrolysis by enzymes and

are illustrated by examples of the hydrolysis of various sugars. The author is able to detect the presence of sucrose in specimens of other sugars, to obtain a quantitative idea of the amount of enzyme present in a given preparation, and to determine the relative molecular weights of various sugars which are hydrolysed by the same enzyme.

C. R. H.

**A Colour Reaction Common to Antiscorbutic Extracts and to Quinol.** N. BEZSSONOFF (*Compt. rend.*, 1921, **173**, 466—468).—

A modified form of the Folin-Denis phenol reagent, prepared by adding its own volume of *N*-sulphuric acid to a solution containing 100 grams of sodium tungstate, 20 grams of phosphomolybdic acid, and 16.6 c.c. of concentrated phosphoric acid per litre, is found to give a blue coloration with plant extracts known to possess antiscorbutic properties and no colour, or at least not a blue colour, with extracts devoid of such properties. It is possible that the action is not due to the antiscorbutic substance itself, but to some polyphenol easily detached from it in solution. Of the numerous phenols examined, quinol was the only one to give the blue colour with this reagent.

When evaporated at 40°, the reagent gave monoclinic crystals having the composition  $17\text{WO}_3 \cdot \text{MoO}_3 \cdot \text{P}_2\text{O}_5 \cdot \text{H}_2\text{O} \cdot 21\text{H}_2\text{O}$ . W. G.

**Methods for Estimating the Amount of Colloidal Material in Soils.** CHARLES J. MOORE, WILLIAM H. FRY, and HOWARD E. MIDDLETON (*J. Ind. Eng. Chem.*, 1921, **13**, 527—530).—

Soil was shaken with water, allowed to settle for twenty-four hours, the turbid liquid then decanted, submitted to centrifugal action, and the resulting opalescent liquid filtered through Pasteur-Chamberlain filter tubes. The colloidal substance collected on the tubes was washed and dried at 110°; it consisted essentially of hydrated aluminium silicate and has been named "ultra-clay." Each 1 c.c. of the ultra-clay absorbed 93 c.c. of dry ammonia gas, but lost this property when heated previously at 1130°. A sample of the soil from which the ultra-clay was obtained absorbed 27.7 c.c. of ammonia per 1 c.c., and 1.4 c.c. of ammonia after previous heating at 1130° (this absorption was probably due to substances other than "ultra-clay") and it is therefore calculated that the soil contained 28.3% of colloidal substance. An exactly similar result was obtained by a method depending on the absorption of malachite green from an ammonium oxalate solution.

W. P. S.



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